Intrazeolite cobalt(II), nickel(II) and copper(II) complexes of 3-formylsalicylic acid for oxidation reactions

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Abstract

Y zeolite encapsulated Co(II), Ni(II) and Cu(II) complexes of 3-formylsalicylic acid were synthesized and characterized by chemical analyses, SEM, XRD, surface area, pore volume and IR, reflectance and EPR spectroscopy with a view to confirm the encapsulation of complexes and to arrive at the composition, structure and geometry of encapsulated complexes. The analytical data indicate a composition corresponding to the binuclear complex of 3-formylsalicylic acid. The characterization data show the absence of extraneous complexes, retention of zeolite crystalline structure and encapsulation in the cavities. The shift of carbonyl-stretching frequencies of both the aldehyde and carboxylate groups of 3-formylsalicylic acid suggests binuclear coordination in the encapsulated complexes. Tetrahedral, octahedral and tetrahedrally distorted square planar symmetries are tentatively assigned to the encapsulated complexes of Co(II), Ni(II) and Cu(II) ions, respectively. Encapsulated Cu(II) complex is catalytically very efficient as compared to other complexes for the partial oxidation of benzyl alcohol and ethylbenzene and is stable to be recycled without much deterioration. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Encapsulation of metal complexes inside microporous supports has emerged as a general technique to increase and control selectivity of catalysts [1]. In addition, the confinement of guest molecules leads to a higher stability by reducing dimerization of active sites. Zeolites are attractive supports for encapsulation as they combine a high thermal and chemical stability with a quite regular, crystalline framework structure. Zeolite complexes posses a number of structural similarities to metalloenzymes and therefore they are expected to mimic enzyme active sites for the catalytic reaction. They are known to catalyze a variety of reactions such as oxidation [2,3], hydrogenation [4], dehalogenation [5], etc.

The early work on zeolite complexes was mainly restricted to monodentate-based complexes [6], but later it was extended to bi- and polydentate ligands [7]. However, binuclear systems in zeolite cavities have not been well explored for the catalytic reactions. Zeolite-encapsulated binuclear complexes can act as model systems for binuclear metalloenzymes. 3-Formylsalicylic acid (fsal) [8] is an attractive ligand system for the synthesis of binuclear complexes with transition metal ions as envisaged in Fig. 1. This study

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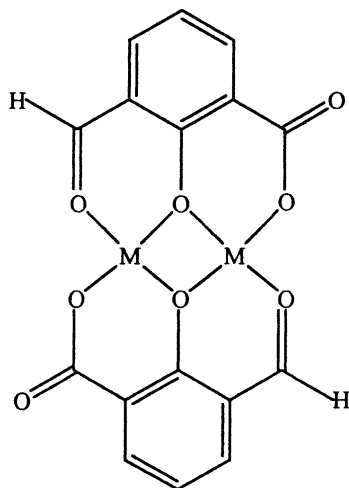
Fig. 1. Binuclear structure of fsal complexes.

aims at the synthesis and characterization of Y zeolite encapsulated Co(II), Ni(II) and Cu(II) complexes of fsal. The catalytic activity studies of the encapsulated complexes for the partial oxidation of benzyl alcohol and ethylbenzene are also reported herein.

2. Experimental

2.1. Synthesis of zeolite-encapsulated complexes of 3-formylsalicylic acid

The sodium form of Y zeolite obtained from Süd-Chemie, India, was used as host material for the encapsulation of complexes. NaY zeolite was ion-exchanged with 0.007 M solution of respective metal chloride to form CoY, NiY and CuY zeolites. The fsal ligand was synthesized according to the method of Duff and Bills [9]. The flexible ligand method [10] was used for the synthesis of complexes in the cavities. In this method, metal-exchanged zeolite was heated with excess of fsal at 125°C for 16 h in a closed glass ampoule to effect complexation. During heating, fsal ligand diffuses into the zeolite and undergoes complexation with metal ions to form complexes which are too large to exit the supercages. The resulting material was soxhlet extracted with methanol to remove unreacted ligand and surface complexes. It was then stirred with sodium chloride

solution to re-exchange the uncomplexed metal ions and finally dried in vacuo at 100°C.

2.2. Characterization techniques

Chemical analyses were carried out [11] by treating a known weight of the sample with concentrated sulfuric acid. The solution was filtered and the residue obtained was analyzed for Si content by determining the loss of weight on HF treatment. The solids after HF treatment were fused with potassium persulfate, then dissolved in water and mixed with sulfuric acid solution. This solution was analyzed for metal contents using a Perkin Elmer 3110 atomic absorption spectrophotometer. The C, H, N content of encapsulated complexes was analyzed by a HERAEUS elemental analyzer. XRD patterns were recorded by a Rigaku D-max C III, X-ray diffractometer using Ni-filtered Cu Kα radiation. BET surface area and total pore volume were measured by nitrogen adsorption at liquid nitrogen temperature using a Micromeritics Gemini 2360 analyzer. Scanning electron micrographs were recorded on a Leica Stereoscan-440. IR spectra in the range 400–4600 cm^{-1} were recorded in KBr pellets using a Shimadzu 8101 FTIR spectrophotometer. Magnetic moment measurements were carried out at room temperature using a Gouy type magnetic balance which was standardized using Co[Hg(SCN)$_4$]. A Cary Win spectrophotometer was used for recording diffuse reflectance spectra at room temperature in the range 200–2000 nm. EPR spectrum of the Cu(II) complex was recorded at liquid nitrogen temperature using a Varian E-109 X/Q bands spectrophotometer.

2.3. Catalytic activity measurements

The catalytic reaction was carried out in a thermostatic reactor of 100 ml volume equipped with a reflux condenser at the neck. The reaction mixture consisting of 50 mg catalyst, 5.0 ml of the substrate (benzyl alcohol or ethylbenzene), 10 ml of benzene and hydrogen peroxide required to keep the oxidant to substrate molar ratio at 2.0 was shaken for 8 h at the specified temperature. After the reaction, the organic layer was separated and the traces of substrate and product in aqueous layer were collected by extracting with diethyl ether. The components were analyzed using a

Chemito-8510 gas chromatograph with SE 30 column and FID detector.

The catalyst in the reaction mixture was filtered, washed with acetone and reused for the reaction at identical conditions to check the recycling ability. After this test, the catalyst was filtered and subjected to IR analysis to identify changes, if any, in the coordination environment.

3. Results and discussion

3.1. Characterization studies

The flexible ligand synthesis scheme leads to the encapsulation of Co(II), Ni(II) and Cu(II) complexes of fsal ligand inside the zeolite pore. The results of chemical analyses of the samples are given in Table 1. The parent NaY zeolite has Si/Al molar ratio of 2.4 which corresponds to a unit cell formula $Na_{56}[(AlO_2)_{56}(SiO_2)_{136}]$. Metal ion exchange at around 39% leads to a metal loading of 3.6–3.9% in zeolite. The unit cell formulae of metal-exchanged zeolites show a metal dispersion of around 11 moles per unit cell.

The analytical data of each complex indicate metal:C:H molar ratios almost close to those calculated for the binuclear structure. However, the presence of minute traces of free metal ions in the lattice could be assumed as the metal content is slightly higher than the stoichiometric requirement. Only a portion of metal ions in metal-exchanged zeolite has undergone complexation and the rest is expected to be removed on re-exchange with sodium chloride solution. But, some of these cation sites in the zeolite lattice might be blocked from solution access by the encapsulated complexes. This shielding effect is

more probable in the present case since the complex loading level is relatively higher than that reported previously [12]. The traces of free metal ions remaining in zeolite, as has been reported in previous studies [13], are unlikely to cause any serious interference in the behavior of the encapsulated complex.

The Si and Al contents in metal-exchanged zeolites and the zeolite complexes are almost in the same ratio as in the parent zeolite. This indicates little changes in the zeolite framework due to the absence of de-alumination in metal ion exchange. The X-ray diffraction patterns of zeolite-containing fsal complexes are similar to those of metal-exchanged zeolites and the parent NaY zeolite. The zeolite crystallinity is retained on encapsulating fsal complexes. Crystalline phases of free metal ions or encapsulated fsal complexes were not detected in any of the patterns as their fine dispersion in zeolite might have rendered them non-detectable by XRD. The SEM photographs of the samples taken before soxhlet extraction show the deposition of complexes on the external surface. However, the absence of extraneous materials in the SEM photographs of finished products indicates the complete removal of surface complexes, which could be accomplished by extended extraction procedures.

Surface area and pore volume values estimated by the low-temperature nitrogen adsorption at relative pressures (P/P_0) in the range 0.05–0.9 are given in Table 2. There is a drastic reduction of surface area and pore volume of zeolites on encapsulating the metal complexes. Since the zeolite framework structure is not affected by encapsulation as shown by the XRD patterns, the reduction of surface area and pore volume provides direct evidence for the presence of complexes in the cavities [14].

FTIR spectra of fsal ligand and zeolite complexes are shown in Fig. 2. The band at around $1000 \, cm^{-1}$

Table 1
Analytical data of zeolites and zeolite complexes

Sample	%Metal	%Si	%Al	%Na	%C	%H	Unit cell formula
NaY		21.76	8.60	7.50			$Na_{56}[(AlO_2)_{56}(SiO_2)_{136}]nH_2O$
CoY	3.72	21.53	8.52	3.35			$Na_{34}Co_{11}[(AlO_2)_{56}(SiO_2)_{136}]nH_2O$
YCo-fsal	1.26	18.63	7.38	6.21	1.99	0.08	
NiY	3.72	21.79	8.62	3.28			$Na_{33.8}Ni_{11.1}[(AlO_2)_{56}(SiO_2)_{136}]nH_2O$
YNi-fsal	2.30	19.89	7.88	5.30	3.46	0.15	
CuY	3.86	21.48	8.48	3.28			$Na_{34.4}Cu_{10.8}[(AlO_2)_{56}(SiO_2)_{136}]nH_2O$
YCu-fsal	2.71	19.43	7.69	5.42	3.60	0.15	

Table 2
Surface area and pore volume data

Sample	Surface area (m^2/g)	Pore volume (ml/g)
NaY	545	0.30
CoY	532	0.30
YCo-fsal	320	0.20
NiY	528	0.30
YNi-fsal	273	0.17
CuY	534	0.30
YCu-fsal	313	0.19

is due to the asymmetric stretching vibration of $(Si/Al)O_4$ units of zeolite host, whereas bending and stretching vibrations of water molecules in zeolite lattice are responsible for the bands at around 1650 and $3500\,cm^{-1}$, respectively. Interpretation of the IR spectra is rendered difficult as the broad zeolite

bands at the region 1000, 1650 and $3500\,cm^{-1}$ obscure some of the bands of metal complexes. The IR spectra of fsal ligand show two strong bands at 1609 and $1668\,cm^{-1}$ which may be assigned to the C=O stretching vibrations in –COOH and –CHO groups, respectively. On complexation, the band at $1609\,cm^{-1}$ is shifted to the region $1550\,cm^{-1}$ as observed in the case of free complex [15]. The band at $1669\,cm^{-1}$ is found to disappear in the spectra of encapsulated complexes, but the new band is masked by zeolite band and hence non-detectable. The shift of these two C=O bands shows that both the carbonyl oxygen atoms are involved in coordination. Thus, IR spectra indicate a binuclear structure for the encapsulated fsal complexes in which phenolic oxygen atoms act as a bridge between two metal ions. Similar structure was reported for the simple complexes of fsal ligand [15,16].
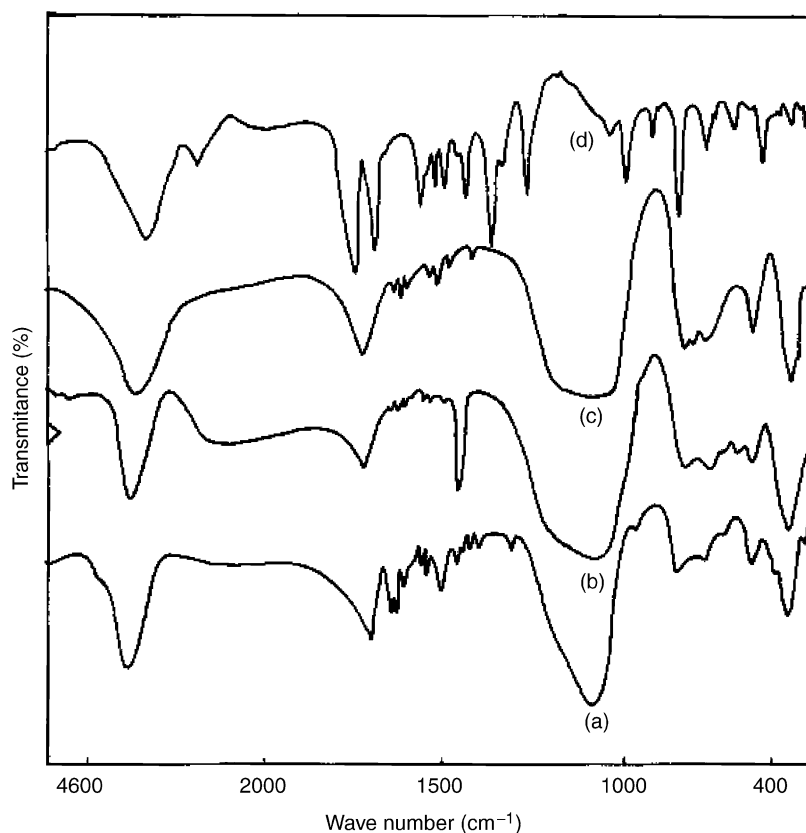

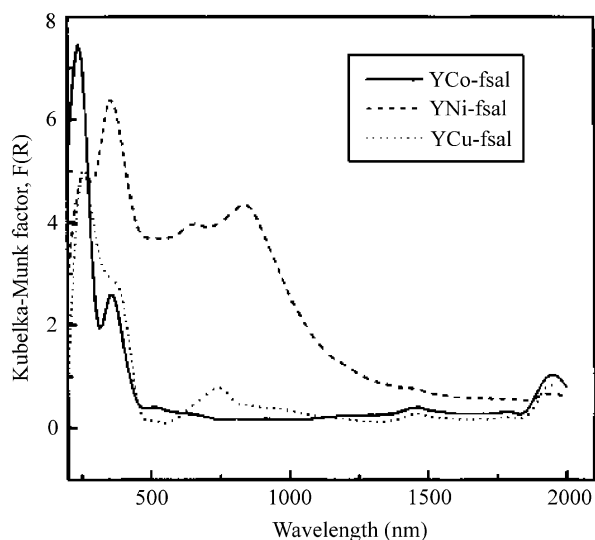Fig. 2. FTIR spectra of fsal and zeolite fsal complexes.

Fig. 3. Electronic spectra of zeolite fsal complexes.

Kubelka-Munk analysis [17] was performed on reflectance data and the results were represented in Fig. 3 as a plot of Kubelka-Munk factor ($F(R)$) against wavelength. The geometries were tentatively assigned for the encapsulated complexes on the basis of absorption bands and room temperature magnetic moment. The bands observed at 15 390 and 19 880 cm^{-1} for YCo-fsal could be attributed to multiple $^4A_2(F) \rightarrow {}^4T_1(P)$ transition, which is characteristic of tetrahedral Co(II) complex [18]. The magnetic moment value of 4.6 BM also indicates a tetrahedral symmetry for the encapsulated Co(II) complex. In the case of YNi-fsal, magnetic moment of 3.4 BM and d–d bands at 11 930, 15 290 and 28 090 cm^{-1} corresponding to $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$, $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ transitions, respectively, are in agreement with those reported for octahedral symmetry [19]. The magnetic moment value of 1.82 BM and broad d–d band at 13 510 cm^{-1} for Cu(II) fsal complex provide little information on the geometry. However, the EPR data for YCu-fsal ($g_\parallel = 2.33$, $A_\parallel = 163 \times 10^{-4}\,cm^{-1}$, $g_\perp = 2.05$, $A_\perp = 31.85 \times 10^{-4}\,cm^{-1}$) suggest a tetrahedrally distorted square planar geometry. The $g_\parallel/A_\parallel$ ratio, a measure of tetrahedral distortion of square planar Cu(II) complexes, is 143 cm which is close to the values reported for a nearly flattened tetrahedral symmetry [20].

3.2. Catalytic testing

The catalytic oxidation of benzyl alcohol and ethylbenzene was studied with zeolite fsal complexes using hydrogen peroxide as the oxidant. Blank reactions performed over NaY zeolite under identical conditions show only negligible conversion indicating that zeolite host is inactive for oxidation. Furthermore, hydrogen peroxide alone is unable to oxidize the substrates in the absence of any catalyst. In representative tests, zeolite complex was filtered out and the filtrate was analyzed for metal content using atomic absorption spectrophotometry. The absence of metal ions in solution phase indicates that no leaching of complexes has occurred during reaction, as they are too intact in the pores. These observations suggest that the oxidations occur due to the catalytic nature of the encapsulated fsal complexes and no significant role is played by either the zeolite support or free complexes.

Zeolite complexes were screened with respect to the activity for the oxidation of benzyl alcohol at 50 °C and the results are shown in Fig. 4. YCu-fsal is distinctly better than other complexes for the oxidation. The activity was found to vary as YCu-fsal > YCo-fsal > YNi-fsal. The oxidation reactions may involve the coordination of oxygen atoms at the vacant sites of metal atom in the complex to form a binuclear oxo-complex [21,22]. This intermediate transfers the coordinated oxygen atoms to the substrate to obtain the product. Thus, the observed catalytic performance of the encapsulated complexes could be attributed to their geometries which govern the availability of vacant coordination sites. The availability of vacant sites in tetrahedrally distorted square planar symmetry
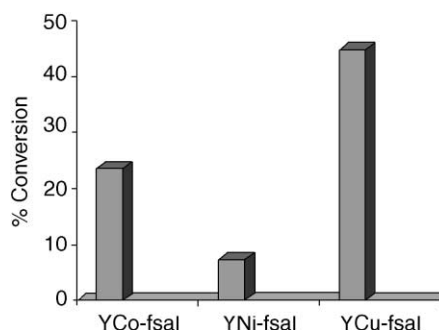

Fig. 4. Activity for benzyl alcohol oxidation at 50 °C.

Table 3
Catalytic activity of YCu-fsal complex

Substrate	Temperature (°C)	% Conversion (w/w)
Benzyl alcohol	50	44.7
Benzyl alcohol	60	61.6
Benzyl alcohol	70	76.5
Ethylbenzene	50	37.8
Ethylbenzene	60	51.2
Ethylbenzene	70	65.6

of Cu(II) complex accounts for the higher activity, whereas tetrahedral symmetry of YCo-fsal and octahedral symmetry of YNi-fsal might have rendered them weakly active. YCu-fsal, the promising sample from the screening test, was further evaluated for catalytic activity for the oxidation of benzyl alcohol and ethylbenzene with hydrogen peroxide at various temperatures and the results are given in Table 3. The conversion in each case was found to increase with increasing reaction temperature.

Transition metal complex-based soluble catalysts are more prone to deactivation by the dimerization of active centers, which is expected to be reduced by encapsulating them in zeolites. YCu-fsal was recycled for the oxidation of benzyl alcohol with hydrogen peroxide with a view to establish the effect of encapsulation on stability. The initial run has showed a conversion of 44.7% and it is only marginally reduced to 42.3% on recycling the catalyst. The results indicate that YCu-fsal complex is almost stable to be recycled for the oxidation of benzyl alcohol without much loss in activity. Thus, the encapsulation of complexes in zeolites is found to increase the life of the catalyst by reducing dimerization due to the restriction of internal framework structure. IR spectrum of the recycled sample is quite similar to that of fresh sample indicating little changes in the coordination of fsal after the oxidation reactions.

It is interesting to note that the oxidation of benzyl alcohol with hydrogen peroxide over zeolite complexes leads to benzaldehyde as the exclusive product. Similarly, acetophenone was the only product formed during the oxidation of ethylbenzene. The absence of further oxidation of these products to benzoic acid shows the ability of zeolite complexes to function as efficient partial oxidation catalysts. Besides overcoming the technical problems in the use of homogeneous catalysts, the attractive features such as sustained reactivity, increased control of partial oxidation, etc. promise a bright future for zeolite-encapsulated complexes.

4. Conclusion

Zeolite-encapsulated binuclear complex of fsal is a novel solid catalyst system for the partial oxidation of organic compounds. Cu(II) complex was found to be very active as compared to Co(II) and Ni(II) complexes indicating the dependence of nature of reaction sites on catalytic activity. These catalyst systems offer structural integrity by having a uniform distribution of the metal complex in the pore structure of the support. The zeolite framework keeps the guest complexes dispersed and prevents their dimerization leading to the retention of catalytic activity. Future work on this system is expected to envisage its industrial applications for partial oxidation reactions.

References

[1] P.K. Dutta, J. Inclus, Phenom. Mol. Recognition Chem. 21 (1995) 215.
[2] I.F.J. Vankelecom, R.F. Parton, M.J.A. Casselman, J.B. Uytterhoeven, P.A. Jacobs, J. Catal. 163 (1996) 457.
[3] N. Herron, J. Coord. Chem. 19 (1988) 25.
[4] D. Chatterjee, H.C. Bajaj, A. Das, K. Bhatt, J. Mol. Catal. 92 (1994) L235.
[5] R. Raja, P. Ratnaswamy, J. Catal. 170 (1997) 244.
[6] G.A. Ozin, C. Gil, Chem. Rev. 89 (1989) 1749.
[7] L.H. Lunsford, Rev. Inorg. Chem. 9 (1987) 1.
[8] M. Tanaka, H. Okawa, I. Hanaoka, S. Kida, Chem. Lett. (1974) 71.
[9] J.C. Duff, E.J. Bills, J. Chem. Soc. (1932) 1987.
[10] N. Herron, Inorg. Chem. 25 (1986) 4714.
[11] S.P. Varkey, C.R. Jacob, Ind. J. Chem. A 37 (1998) 407.
[12] N. Herron, G.D. Stucky, C.A. Tolman, J. Chem. Soc., Chem. Commun. (1986) 1521.
[13] H. Diegruber, P.J. Plath, G. Schulz-Ekloff, M. Mohl, J. Mol. Catal. 24 (1984) 115.
[14] K.J. Balkus, A.G. Gabrielov, J. Inclu. Phenom. Mol. Recognition Chem. 21 (1995) 159.
[15] M. Tanaka, M. Kitaoka, H. Okawa, S. Kida, Bull. Chem. Soc. Jpn. 49 (1976) 2469.
[16] M. Tanaka, H. Okawa, T. Tamura, S. Kida, Bull. Chem. Soc. Jpn. 47 (1974) 1669.

[17] S.K. Tiwary, S. Vasudevan, Inorg. Chem. 37 (1998) 5239.

[18] A.B.P. Lever, Inorganic Electronic Spectroscopy, Elsevier, Amsterdam, 1968.

[19] N.N. Greenwood, A. Earnshaw, Chemistry of the Elements, Pergamon Press, Oxford, 1984.

[20] U. Sakaguchi, A.W. Addison, J. Chem. Soc., Dalton Trans. (1979) 600.

[21] R.A. Sheldon, J.K. Kochi, Metal-catalysed Oxidations of Organic Compounds, Academic Press, New York, 1981.

[22] B. Meunier, Bull. Soc. Chim. Fr. (1986) 578.