Novel color isomerism and catalytic activities of Cu(salen) complex encapsulated in a zeolitic matrix

Subratanath Koner*

Catalysis Division, National Chemical Laboratory, Pune 411 008, India

The green zeolite encapsulated Cu(salen) complex on treatment with MeCN turns red and is found to be catalytically active towards oxidation reactions whereas the green species is inactive.

The development of efficient biomimetic oxidation catalysts containing metal complexes of porphyrins, phthalocyanines, Schiff-bases, *etc.* which mimic the active sites of metalloenzymes has received a lot of attention.[1] The oxidation reactions catalyzed by metal complexes are often impeded due to oxidative degradation of the complex and/or the formation of μ-oxo dimers.[1c] Several strategies, *viz.* encapsulation of those complexes within zeolitic[2,3] or polymeric matrices[4] or intercalation in clays,[2] have been adopted to enhance the stability and reactivity of such catalysts. It is now well understood that encapsulation of these complexes in zeolitic hosts can enhance the catalytic performance of the complexes in comparison to their homogeneous counterparts used in solution.[1c]

Here, we report the preparation, novel physicochemical properties and unique catalytic behavior of a zeolite (NaY) encapsulated Cu(salen) [salen = *N*,*N*′-bis(salicylaldehyde)-ethylenediimine] complex [Cu(salen)-NaY].

To prepare Cu(salen)-NaY, 2 g of calcined Cu-NaY† zeolite was mixed with 2 g of salen and placed in a sealed glass tube containing dry N_2 and heated at 150 °C with occasional stirring for 5–6 h. The green mass thus formed was then pulverized and subjected to Soxhlet extraction with MeOH and Me_2CO. The extracted green solid was then stirred with the portions of fresh MeCN several times. To our surprise during the stirring with MeCN the green mass transformed in to a red solid within a few min whereas treatment of Cu(salen) with MeCN or recrystallization of the complex from the same solvent gave no such color change. Although there is ample evidence of metal complexes recrystallized from different solvents giving different colors owing to the formation of different isomers or conformers[5,6] the present type of color isomerism among zeolite encapsulated metal complexes is rarely observed. No color change is observed when the green species is treated with other sovlents such as EtOH, Pr^iOH, CH_2Cl_2, $CHCl_3$, *etc.* Elemental analysis showed the Cu content of this solid was *ca.* 0.06%, which corresponds to encapsulation of *ca.* 26 molecules of [Cu(salen)] per 100 supercages in this solid. The Cu content of the green solid is virtually the same.

A relatively weak band in the visible region in the electronic spectra of the prepared catalysts and pure complex {590 nm for [Cu(salen)] and Cu(salen)-NaY(green); 558 nm for Cu(salen)-NaY(red)} is assigned to d–d transitions whereas two fairly strong bands appearing in the range 410–280 nm are assigned to ligand charge transfer bands {370 and 286 nm for the red and green species and 406 and 355 for the [Cu(salen)] complex} (Fig. 1).[5] All the prominent IR bands for ligand vibrations appearing in the region 1700–1250 cm^{-1} of the [Cu(salen)] species are also present in Cu(salen)-NaY. The ligand vibration bands in the other regions are obscured by the presence of zeolitic vibration bands. The principal *g* values calculated by usual methods from EPR spectra (Fig. 2) are in agreement with those reported for Cu^II Schiff base complexes.[7] The $g_{\parallel}$ and $g_{\perp}$ values of the red and green species of Cu(salen)-NaY and for

[Cu(salen)] are 2.189, 2.178, 2.176 and 2.041, 2.039, 2.044, respectively.

All the above results convincingly demonstrate the presence of the [Cu(salen)] chromophore in both varieties of Cu(salen)-NaY catalysts. The shifting of the d–d transition band to shorter wavelength in electronic spectra of the red species in comparison to the green species clearly indicates that the axial ligand field around the Cu^II ion is weaker in the former.[6b,8b] EPR spectra are in accord with this as $g_{\parallel}$ values of the red species are higher than that of the green species whereas the $g_{\perp}$ values are almost the same. It is well documented that a decrease of axial ligand interaction with Cu^II in these types of complexes leads to a red-shift of d–d transition bands and an increase in $g_{\parallel}$.[6b,8] It is also noteworthy that the resolution of IR spectral bands for ligand vibrations of the red species is higher than the green species suggesting that the Cu(salen) moiety in the red species is more comfortably enclosed inside the zeolitic supercage than in the green species; which also indirectly indicates that the interaction between the Cu(salen) moiety and the zeolitic matrix in the red species is much weaker than in the green species. Therefore, it can be proposed that in the green species, Cu^II
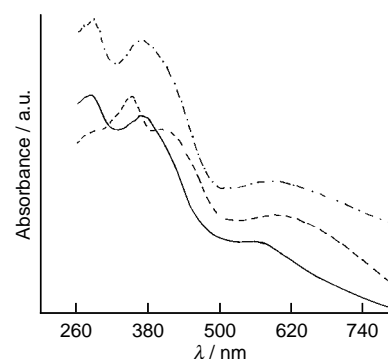
Fig. 1 UV–VIS diffuse reflectance spectra of Cu(salen)-NaY(red) (———) Cu(salen)-NaY(green) (-·-·--) and Cu(salen) (- - - -)
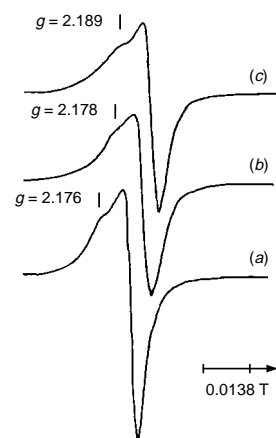
Fig. 2 EPR spectra of Cu(salen) (*a*), Cu(salen)-NaY(green) (*b*) and Cu(salen)-NaY(red) (*c*)

Table 1 Catalytic performance of zeolite encapsulated Cu(salen)

Catalyst	Substrate	t/h	Conversion (mass%)	Product
Cu(salen)-NaY(red)	Norbornene	3	23.1	*exo*-Epoxynorbornane[a]
		12	66.7	*exo*-Epoxynorbornane[a]
	1-Naphthol	12	16.8	1,4-Naphthoquinone[a]
Cu(salen)-NaY(green)	Norbornene	12	0.1	—[b]
	1-Naphthol	12	0.2	—[b]

[a] Selectivity = 100 (mass%). [b] No expected oxidized products are detected.

forms weak Cu–O bonds with zeolitic oxygen to give either square-pyramidal or octahedral geometry around the Cu^{II} ion, which upon treatment with MeCN becomes square planar. The formation of weak Cu–O bonds between the Cu^{II} ion and zeolitic oxygen can not be ruled out since recently it has been shown by single crystal X-ray analysis that Cu(salen) forms dimers through weak Cu–O (O-salen) bonds in the solid state.[5]

The epoxidation of norbornene and hydroxylation of 1-naphthol were carried out in a glass batch reactor using TBHP (*tert*-butyl hydroperoxide) as oxidant. MeOH was used as solvent for Cu(salen)-NaY(green) while MeCN was used for Cu(salen)-NaY(red). In a typical reaction, 0.1 g of catalyst was slurried in a batch reactor with 10 g of MeCN or MeOH. To this, 0.5 g of oxidant was added and the mixture allowed to equilibrate at 50 °C in oil bath. After *ca.* 10 min the substrate was added and products collected at different time intervals and identified and quantified by GC and verified by GC–MS.

Results for both reactions (Table 1) established that the Cu(salen)-NaY(red) catalyst showed excellent product selectivity as well as activity towards oxidation reactions with exclusively one oxidized product being obtained in each case. Selectivity of products to this extent is rare among zeolite encapsulated metal complex catalysts. For the 1-naphthol hydroxylation reaction 1,4-naphthoquinone is selectively obtained among the three possible products (1,4-naphthoquinone, 1,4-dihydroxynaphthalene, 1,2-dihydroxynaphthalene)[9] whereas for norbornene only *exo*-epoxynorbornane is obtained, where *exo*- and *endo*-epoxynorbornane, cyclohexene-4-carbaldehyde and norcamphor are all possible products.[10] On the other hand Cu(salen)-NaY(green) does not show any activity towards these reactions. It should be noted that Cu is not detected in the liquid phase of the reaction mixtures (the solid catalyst is separated from the mixture by filtration at *ca.* 50 °C) after completion of experiment. Therefore, the Cu complex is not leached from the catalysts during reaction.

In conclusion, it can be stated that the catalytic activity of Cu(salen)-NaY changes dramatically with change in the coordination geometry around the Cu^{II} ion in the zeolite. The Cu(salen)-NaY(red) catalyst where Cu^{II} ion appears to possess vacant axial positions shows activity[1e,5] towards oxidation reactions whereas the green variety, where Cu^{II} ion is either five- or six-coordinate, is inactive. Further this work is a novel example where a metal complex encapsulated in a zeolitic matrix shows color isomerism upon treatment with a specific solvent.

Notes and References

* Present Address and Address for Communication: Biomolecular Engineering Department, National Institute of Bioscience and Human Technology, 1-1 Higashi, Tsukuba, Ibaraki 305, Japan. Fax: +81-298-54-6161; E-mail: skoner@ccmail.nibh.go.jp

† Cu-NaY was prepared by stirring a slurry of NaY in Cu(NO$_3$)$_2$ solution [1 g NaY with 0.25 g Cu(NO$_3$)$_2$ dissolved in 200 ml of water] at room temp. In order to control the quantity of Cu^{II} exchange in NaY-zeolite a relatively dilute Cu(NO$_3$)$_2$ solution was used and the stirring time was fixed at 30 min. The Cu content in the solid is found to be *ca.* 0.075%. Cu(salen)-NaY(green) was prepared following the same procedure as above (main text) avoiding treatment with MeCN. The catalysts were calcined at 120 °C for 8–10 h in dry N$_2$ before use in reactions. To re-exchange the unreacted Cu^{II} present in both the green and red solids by Na$^+$ ions they were repeatedly stirred in NaNO$_3$ solution for several hours.

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