# Chromotropism of Cr(salen) moiety in zeolite matrix: synthesis, characterization and catalytic activity study of Cr(salen)-NaY hybrid catalyst

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## Abstract

The $[Cr(salen)]^+$ [salenH$_2$ = $N,N'$-bis(salicylaldehyde)-ethylenediimine] complex moiety is immobilized in NaY matrix to obtain a new hybrid catalytic system. The resulting yellow colored zeolite immobilized Cr(salen) catalyst on washing with CH$_3$OH and H$_2$O turns to light grey. The spectroscopic measurements showed that the interaction between axially coordinated H$_2$O and Cr(III) in $[Cr(salen)(H_2O)_2]^+$ moiety becomes weaker on the entrapment of the complex moiety in Y zeolite supercage. A good catalytic performance of the newly prepared hybrid catalyst was observed in epoxidation reaction of norbornene and styrene.
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## 1. Introduction

The preparation of new functional materials by immobilizing the selective chemical compound in zeolitic matrices, which are expected to have exotic properties like catalysis, photoredox or chromotropism has received a lot of attention [1–4]. Recently, metal complexes of porphyrins, phthalocyanines, Schiff-bases, etc. have been encapsulated into zeolitic matrix for the development of efficient biomimetic oxidation catalysts which have acted as the functional mimic of metalloenzymes. The oxidation reactions catalyzed by metal complexes are often impeded due to oxidative degradation of complex and/or the formation of μ-*oxo* dimers [5]. Several strategies, viz. encapsulation of those complexes within zeolitic [6] or

polymeric matrices [7] or intercalation in clays [8], 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. On immobilization of certain types of organic compounds in zeolite matrices showed brilliant color change [9]. The organic dye molecules are immobilized in zeolite or molecular sieve to prepare sensor [10]. Detail studies on the photochemical and photophysical properties of ruthenium complexes encapsulated in zeolite matrices have been undertaken by several groups [11]. It has been found that these properties of neat metal complexes have dramatically changed on immobilization in zeolites. In an earlier communication, we have reported that the complex Cu (salen) [salenH$_2$ = $N,N'$-bis(salicylaldehyde)-ethylenediimine] encapsulated in Y zeolite shows novel

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color isomerism (green to red) on treatment of specific solvent [12]. In this study, we will report the investigation on chromotropism of complex Cr(salen) immobilized in zeolite matrix and the catalytic properties of the prepared hybrid catalysts.

## 2. Experimental

### 2.1. Materials

The zeolite NaY ($SiO_2/Al_2O_3$ = 5.7) was purchased from Tosoh Company Ltd., Japan used for immobilization. The ligand *N,N'*-bis(salicylaldehyde)-ethylenediimine (salenH$_2$) was prepared by following the reported procedure [13]. The other chemicals used were of AR quality. The complex [Cr(salen)(H$_2$O)$_2$]Cl was prepared by following the method put forward by Yamada and Iwasaki [14].

### 2.2. Physical measurement

Infrared and electronic spectra were measured on Perkin-Elmer 783 and Hitachi U 3400 spectrophotometer, respectively. The catalytic reaction products were quantified by Aimil 5700 Nucon gas chromatograph and verified by Shimadzu QP 5000 GCMS. EPR spectra were measured on Varian E-112 EPR spectrometer at room temperature. The microwave frequency for EPR measurements was fixed at 9.45 GHz. The X-ray powder diffraction measurements were done on PW 1730/1710 Philips XRD diffractometer. The chromium content of the samples was estimated by Varian Techtron AA-575 ABQ atomic absorption spectrophotometer.

### 2.3. Preparations

#### 2.3.1. Preparation of Cr-NaY

For incorporation of Cr(III) into zeolite matrix an aqueous solution of CrCl$_3$·6H$_2$O (1.45 g) was stirred with NaY (8.29 g) in suspension for ca. 5 h. During stirring, the white mass turns to green. The solid mass was then filtered and washed thoroughly with copious amount of deionized water (using soxhlet) and dried under vacuum to give a light-green powder. The Cr-NaY zeolite thus produced was used for immobilization work.

### 2.3.2. Immobilization of [Cr(salen)]$^+$ in NaY

Five grams of Cr-NaY was taken in a mixture of ethylene glycol, water and methanol (30, 30 and 90 ml, respectively). 1.7 ml ethylenediamine (25 mmol) and 5.25 ml salicylaldehyde (50 mmol) were added to this. The mixture was then heated in an oil bath to 110 °C and kept at this temperature for half an hour. The whole mass was cooled and 1.665 g of sodium carbonate anhydrous was added to this in portions. This was then refluxed for 4 h. On filtration, an orange solid was obtained which was washed successively with methanol and distilled water using a soxhlet. The solid product was dried under vacuum to produce a light grey powder. The catalysts thus obtained will be referred as Cr(salen)-NaY hereinafter.

### 2.4. Catalytic reactions

The catalytic reactions were undertaken in glass batch reactor. In a typical reaction, 1 g of the substrate was taken in 10 ml of CH$_3$CN (or CH$_2$Cl$_2$ in case of styrene). Fifty milligrams of the catalyst was added to this. This was then equilibrated to 40 °C in an oil bath. One milliliter 30% H$_2$O$_2$ solution was added to this with continuous stirring. The products of the oxidation reactions were collected at different time intervals and were identified and quantified by GC and verified by GCMS.

## 3. Results and discussion

Kochi and co-workers [15] have shown that the complex [Cr(salen)(H$_2$O)$_2$]PF$_6$ can act as efficient catalyst in epoxidation of alkenes. It is proposed that the complex transfers the *oxo*-group to oxidize the substrate through formation of intermediate O=Cr(salen)PF$_6$. We have earlier immobilized this chromium complex moiety in MCM-41 matrix for improvement of its catalytic performance [16].

In the case of Cr(salen)-MCM-41, immobilization was undertaken simply by dissolving the complex [Cr(salen)(H$_2$O)$_2$]Cl in H$_2$O and stirring MCM-41 in suspension for 24 h [16]. Such process of immobilization is unrealistic in the case of NaY because it will then give only the exchanged product where the complex moiety will be attached to the surface of zeolite. The complex in this process will never be able

to enter into the supercage of the zeolite that is rather our goal. On the other hand, solution synthesis route (vide Section 2) gave us a very interesting hybrid material viz. Cr(salen)-NaY in terms of its catalytic and physicochemical properties.

Atomic absorption spectrometric analysis showed chromium content of Cr(salen)-NaY to be ca. 0.475% (by weight). The X-ray powder diffraction analysis of NaY and Cr(salen)-NaY showed that the crystallinity of the zeolite matrix almost remains intact after formation of complex in it. The surface area measurement gives the valuable information about immobilization of the complex in zeolite matrix [17]. Nitrogen sorption experiment showed a significant decrease in the surface area of the immobilized materials in comparison to the original NaY zeolite in the present case. Nitrogen is generally adsorbed in the micropores as well as the outer surface of the zeolite. So if the complex CuL occupies the pores of NaY zeolite in CuL-NaY it is expected that the amount of adsorbed gas by the catalyst will be low. Indeed this happens in the case of CuL-NaY. The total surface area of the original NaY was $767 \, m^2 \, g^{-1}$; on immobilization of the complex into it this value decreases to ca. $550 \, m^2 \, g^{-1}$.

The IR spectra of the pristine $[Cr(salen)(H_2O)_2]Cl$ complex, Cr(salen)-NaY and NaY were measured. An intense band is appearing at ca. $1640 \, cm^{-1}$ in IR spectrum of both the neat complex and Cr(salen)-NaY. This band can be assigned as the characteristic band for azomethine group of salen while it is coordinated with Cr(III) [18]. The IR band of azomethine group for free salenH$_2$ occurs at frequencies higher by ca. $10 \, cm^{-1}$. But as zeolite-based materials usually adsorbs H$_2$O this band often overlapped with the H–O–H bending band appearing in this region. The bending band of H$_2$O can be eliminated from IR spectrum on careful drying of the zeolite. In this study, dehydrated NaY and Cr(salen)-NaY were collected from TG instrument after complete dehydration of samples and immediately they were mixed with nujol. It has been found that almost no or only very little amount of H$_2$O gets adsorbed in this process, once the sample is mixed with nujol no H$_2$O molecule is adsorbed by the zeolite for several days. No IR bands for zeolite or nujol are appearing in this region. Therefore, appearance of absorption band at $1640 \, cm^{-1}$ in IR spectrum of Cr(salen)-NaY is indicating the presence of Cr(salen) moiety in it (Fig. 1). The vibration bands of the host

zeolite as well as nujol obscure the IR bands of the complex in other regions of Cr(salen)-NaY.

The electronic spectra of the species Cr(salen)-NaY and $[Cr(salen)(H_2O)_2]Cl$ complex are given in Fig. 2. The peaks appearing at 504 and 420 nm in electronic spectra of $[Cr(salen)(H_2O)_2]Cl$ are interpreted as the d–d and ligand charge transfer bands. The comparison of electronic spectra of the species Cr(salen)-NaY and the $[Cr(salen)(H_2O)_2]Cl$ complex showed that the characteristic band (ca. 504 nm) for d–d transition of $[Cr(salen)]^+$ complex moiety is shifted to the shorter wavelength region (blue shift) and merged with the charge-transfer band in case of the immobilized complex. The Cr(salen)-NaY shows only one well-defined peak at 390 nm but it has a long tail in the visible region.

The EPR spectra of Cr-NaY, Cr(salen)-NaY and $[Cr(salen)(H_2O)_2]Cl$ were given in Fig. 3. The principal g-value for $[Cr(salen)(H_2O)_2]Cl$ and Cr-NaY calculated by using the standard procedure from their EPR spectrum was found to be 1.968 and 1.969, respectively [19,20]. The line shape of EPR spectrum of the $[Cr(salen)]^+$ complex moiety changes drastically on immobilization of it into the NaY matrix indicating that the coordination environment around chromium ion of the complex moiety in NaY matrix is completely different from the neat $[Cr(salen)(H_2O)_2]Cl$ complex. The comparison of the spectra of the above mentioned three species showed that a new EPR line appears at ca. 3016 G for Cr(salen)-NaY in addition to the original lines appeared in the case of $[Cr(salen)(H_2O)_2]Cl$ or Cr-NaY at ca. 3276 G (Fig. 3). The new line can be assigned as the EPR line of $[Cr(salen)]^+$ present in Cr(salen)-NaY while the original line appears at ca. 3285 G for the free Cr(III) ions. It is noteworthy that elemental analysis of Cr(salen)-NaY showed only about 50% of Cr(III) ions form the $[Cr(salen)]^+$ moiety during complexation with salenH$_2$ whereas remaining portion of the Cr(III) ions remained as it is in Cr(salen)-NaY. Therefore, appearance of new line in EPR spectrum is not inconsistent with the elemental analysis result. The shifting of EPR line of $[Cr(salen)]^+$ moiety in the lower field region in prepared catalyst in comparison to the corresponding line of $[Cr(salen)(H_2O)_2]Cl$ is probably due to the decrease of axial ligand field around Cr(III) ion on immobilization. It is well documented that a decrease of axial ligand interaction with central metal ion in these
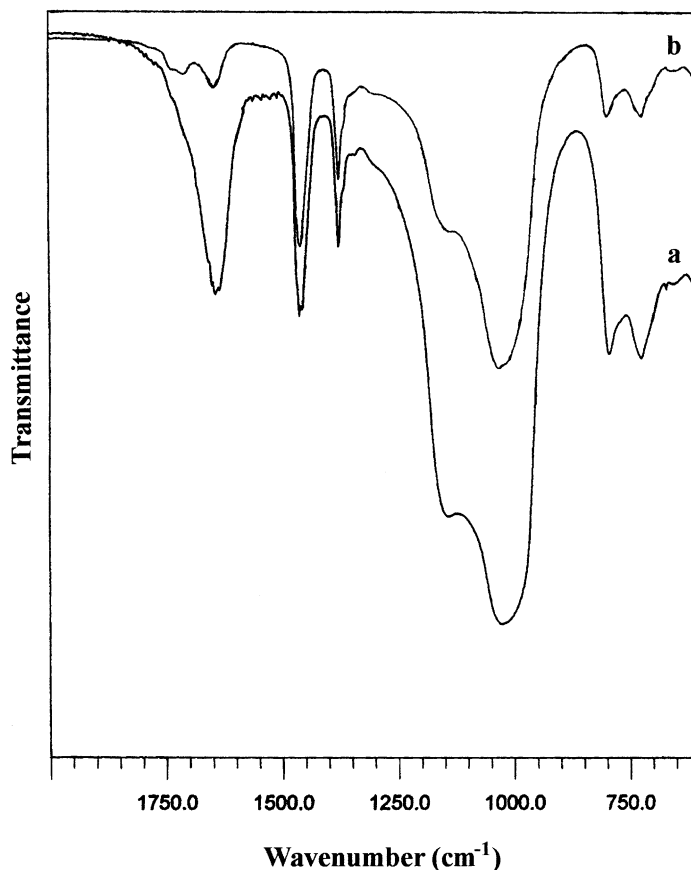
Fig. 1. The IR spectra of Cr(salen)-NaY (a) and NaY (b).

types of complexes leads to blue shift of d–d transition in electronic spectra and an increase of *g*-value [21]. Therefore, shifting of EPR line is in accord with this as less axial interaction of ligand is apparent when the complex is entrapped in the NaY supercage. It should be noted here that the similar type of structural change of metal complex moiety was also observed in the case of immobilization of Cu(salen) in Y zeolite matrix [12,22].

The epoxidation of norbornene and styrene was carried out to test the catalytic performance of the prepared hybrid materials. The results of catalytic reactions are given in Table 1. The results of both reactions established that the Cr(salen)-NaY showed a remarkable activity towards oxidation reactions. In case of epoxidation of norbornene, it showed excellent selectivity also by giving only one product where *exo*- and *endo*-epoxynorbornane, cyclohexane-4-carbaldehyde and norcamphor are all possible products [23]. This type of selectivity in the reactions is important for application of the prepared catalyst in the industry to minimize the undesired waste products. To test if the chromium complex is leaching out from the catalyst, the following experiment was performed. The catalyst was taken in a 10 ml of $CH_3CN$ or $CH_2Cl_2$ and 1 ml of 30% $H_2O_2$ (aqueous) solution was added to it and the final mixture was stirred for 12 h at 50 °C in an oil bath. The mixture was then filtered hot. The filtrate neither shows any activity towards oxidation reactions nor the atomic absorption spectroscopic analysis shows the presence of Cr in the filtrate. Therefore, it can be concluded that the chromium complex is not leached from the catalysts during oxidation reaction.

Table 1
Catalytic performance of Cr(salen)-NaY[a]

| Catalyst | Reaction time (h) | Conversion (mass%) | Product distribution (mass%) | |
|---|---|---|---|---|
| | | | *exo*-Norbornene epoxide | Styrene epoxide |
| Cr(salen)-NaY | 6 | 35 | 25.9 | – |
| | 24 | 50 | 42.4 | – |
| | 6 | 60 | – | 53.5 |
| | 24 | 70 | – | 59.3 |
| [Cr(salen)(H$_2$O)$_2$]Cl | 24 | 65 | 57[b] | – |
| | 24 | | – | 22 |
| Cr-NaY | 24 | No detectable activity[c] | | |
| NaY | 24 | No detectable activity[c] | | |

[a] No Cr leaching during reaction.

[b] Product includes *exo-* and *endo*-norbornene epoxide.

[c] NaY and Cr-NaY showed no catalytic activity towards epoxidation of norbornene and styrene.
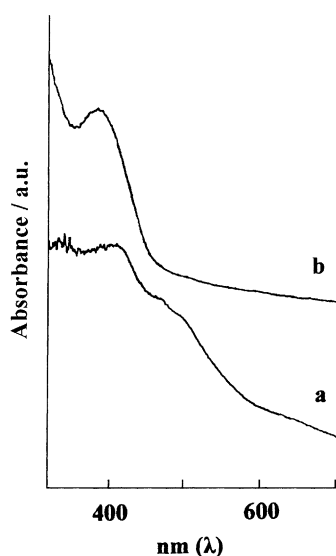


Fig. 2. The UV-Vis spectra of [Cr(salen)(H$_2$O)$_2$]Cl (a) and Cr(salen)-NaY (b).



Fig. 3. The EPR spectra of [Cr(salen)(H$_2$O)$_2$]Cl (a), Cr(salen)-NaY (b) and Cr-NaY (c).

It is clear from the above discussion that the species Cr(salen)-NaY shows an interesting chromotropism on immobilization in the NaY matrix. Spectroscopic measurements showed the interaction between the Cr(III) ion and the axial ligands H$_2$O decreases on immobilization of the complex moiety in NaY. As a result, the in-plane ligand field around Cr(III) increasing in Cr(salen)-NaY. Consequently, the d–d transiti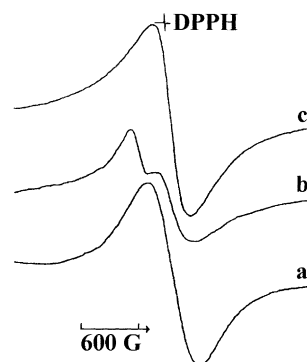on band of the complex moiety shifted to the shorter wavelength region and we observed the color change. This loosely bound axial ligand facilitates the *oxo-* transfer reaction and hence increasing the catalytic performance of Cr(salen) moiety in NaY. The catalytic performance of the present catalyst is comparable to a similar type of catalyst Cr(salen)-MCM-41 reported earlier [16].

## Acknowledgements

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