

# Immobilization of Cr(salen) moiety in MCM-41 and studies on its catalytic properties

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## Abstract

The  $[\text{Cr}^{\text{III}}(\text{salen})]^+$  complex moiety is immobilized in MCM-41 matrix to obtain a new hybrid catalytic system; to test its activity, epoxidation of norbornene and hydroxylation reaction of 1-naphthol are carried out by using TBHP (*tert*-butylhydroperoxide) as oxidant. © 1999 Elsevier Science B.V. All rights reserved.

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Development of efficient biomimetic heterogeneous oxidation catalysts containing metal complexes (such as Schiff base, phthalocyanine or porphyrin complexes) which mimic the catalytic activities of metalloenzymes has received a lot of attention [1,2]. One such approach is the encapsulation/incorporation of metal complexes in zeolitic, polymeric or clay matrices where the complex is believed to be active like the active sites of metalloenzymes [2]. It is now well understood that the zeolite encapsulated metal complexes can show better catalytic performance (such as activity, selectivity, etc.) than the corresponding pure complexes used in homogeneous reactions in solution [3]. However, there are instances where excess inclusion of

complex in Y-zeolitic matrix makes the catalyst practically inactive due to the blockage of pores and channels of its host. Recently, we developed a new hybrid catalytic system consisting of Cu(salen) [salen = *N,N'*-bis(salicylaldehyde)-ethylenediimine] complex where loading of the complex was deliberately kept at a relatively lower concentration [4]. In the present study, we immobilized  $[\text{Cr}^{\text{III}}(\text{salen})]^+$  moiety in a relatively larger pore aluminosilicate molecular sieve MCM-41 (the immobilized species hereinafter designated as Cr(salen)MCM-41).

The complex  $[\text{Cr}(\text{salen})(\text{H}_2\text{O})_2]\text{Cl}$  was prepared by following the reported procedure [5]. The immobilization of this complex in MCM-41 was done by dissolving the complex in  $\text{H}_2\text{O}$  and stirring MCM-41 in suspension for 24 h. The red colored solid was then filtered and washed first with  $\text{H}_2\text{O}$  and then with  $\text{CH}_3\text{CN}$  by Soxhlet extraction technique until the extracted solvent becomes colorless. During this

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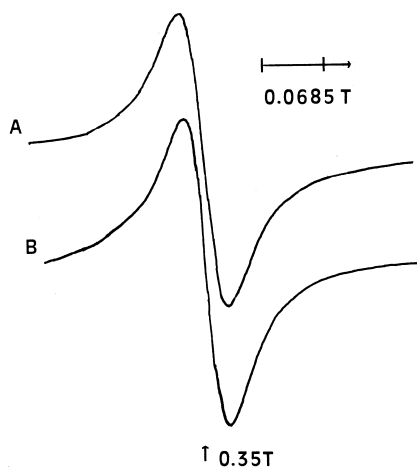


Fig. 1. EPR spectra of  $[\text{Cr}(\text{salen})(\text{H}_2\text{O})_2]\text{Cl}$  (A) and  $\text{Cr}(\text{salen})\text{MCM-41}$  (B).

extraction, the absorbed complex on catalysts surface seems to be removed. The prepared complex and the catalyst were then characterized by several techniques. Atomic absorption spectrometric analysis showed Cr content of this solid was ca. 0.736%. Elemental analyses (carbon and nitrogen) and TG-DTA measurement also support this. The aluminosilicate MCM-41 was prepared according to the literature procedure [6].

The comparison of electronic spectra of  $[\text{Cr}(\text{salen})(\text{H}_2\text{O})_2]\text{Cl}$  and  $\text{Cr}(\text{salen})\text{MCM-41}$  shows that the characteristic band (ca. 490 nm) for d–d transition of  $[\text{Cr}^{\text{III}}(\text{salen})]^+$  complex moiety is

present in the case of  $\text{Cr}(\text{salen})\text{MCM-41}$ . All the prominent IR bands for ligand vibrations appearing in the region  $1600\text{--}1300\text{ cm}^{-1}$  of the  $[\text{Cr}^{\text{III}}(\text{salen})]^+$  species are also present in  $\text{Cr}(\text{salen})\text{MCM-41}$ . The ligand vibration bands in the other regions are obscured by the presence of vibration bands of host molecular sieve. These results convincingly demonstrate the presence of  $[\text{Cr}^{\text{III}}(\text{salen})]^+$  chromophore in the prepared catalyst. The principal  $g$  value of  $[\text{Cr}(\text{salen})(\text{H}_2\text{O})_2]\text{Cl}$  and  $\text{Cr}(\text{salen})\text{MCM-41}$ , calculated by using the standard procedure from their EPR spectra [7,8], is found to be 1.9650 and 1.9533, respectively (Fig. 1). The difference in  $g$  values clearly indicates that the  $[\text{Cr}^{\text{III}}(\text{salen})]^+$  moiety is little distorted in  $\text{Cr}(\text{salen})\text{MCM-41}$  [7,8], which is not inconsistent with the fact that the said chromophore confines itself into the channel of the molecular sieve during immobilization.

Two test reactions, viz. oxidation of norbornene and hydroxylation of 1-naphthol are carried out in a glass batch reactor at  $60^\circ\text{C}$  using  $\text{CH}_3\text{CN}$  as solvent. TBHP (*tert*-butylhydroperoxide) is used as oxidant for hydroxylation of 1-naphthol as well as the oxidation of norbornene. In a typical reaction, 0.1 g of catalyst is placed in a batch reactor as slurry in 10 g of  $\text{CH}_3\text{CN}$ . To this, 0.5 g of oxidant is added and the mixture is allowed to equilibrate at  $60^\circ\text{C}$  in oil bath. After ca. 20 min, substrate is added.

Table 1  
Catalytic performance of  $\text{Cr}(\text{salen})\text{MCM-41}^a$

Catalyst	Reaction time (h)	Conversion (mass%)	Product distribution (mass%)				
			Norbornene epoxidation		Naphthol hydroxylation		
			Exo	Endo	NQ	1,4-DHN	1,2-DHN
$\text{Cr}(\text{salen})\text{MCM-41}$	3	30	22.2	–	–	–	–
	12	60	43.3	10.1	–	–	–
$[\text{Cr}(\text{salen})(\text{H}_2\text{O})_2]\text{Cl}$	12	39	13.0	12.1	–	–	–
MCM-41	12		No detectable activity				
$\text{Cr}(\text{salen})\text{MCM-41}$	12	19.8	–	–	16.2	–	–
$[\text{Cr}(\text{salen})(\text{H}_2\text{O})_2]\text{Cl}$	12	10.2	–	–	5.8	1.74	1.25
MCM-41	12		No detectable activity				

<sup>a</sup>No Cr leaching during reaction. NQ = 1,4-naphthoquinone, 1,4-DHN = 1,4-dihydroxynaphthalene, 1,2-DHN = 1,2-dihydroxynaphthalene.

Products are collected at different time intervals and are identified and quantified by GC and verified by GC–MS. The results of these reactions are given in Table 1. It should be noted that the catalyst can be reused at least five times in cycle without having any loss of activity. Further Cr 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 Cr complex is not leached from the catalysts during reaction.

Results for both reactions (Table 1) established that immobilization of  $[\text{Cr}^{\text{III}}(\text{salen})]^+$  complex moiety into the MCM-41 can give higher activity as well as product selectivity towards oxidation reactions. Indeed, the 1-naphthol hydroxylation reaction shows excellent selectivity by giving selectively only one oxidized product among the three possible products [6]. This type of reaction has enormous industrial importance for minimizing the undesired waste products.

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