

# Heterogenization of three homogeneous catalysts: A comparative study as epoxidation catalyst



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## ABSTRACT

Three homogeneous catalysts,  $\text{Mn}^{\text{I}}\text{Cl}\cdot 2\text{H}_2\text{O}\cdot (1.2\text{H}_2\text{O})$  (HmC-1),  $\text{Fe}^{\text{I}}(\text{NO}_3)\cdot 3\text{H}_2\text{O}$  (HmC-2) and  $\text{Co}^{\text{I}}(\text{NO}_3)\cdot 2\text{H}_2\text{O}$  (HmC-3) [ $\text{L}^{\text{I}} = N,N'$ -ethylenebis(3-formyl-5-methylsalicylaldehyde)] have been synthesized and characterized. The catalytic activity of HmC-1, -2 and -3 for epoxidation of alkenes has been investigated in the presence of terminal oxidant *tert*-butyl hydrogen peroxide (TBHP), in two solvents  $\text{CH}_3\text{CN}$  and  $\text{CH}_2\text{Cl}_2$ . Epoxidation of alkenes catalyzed by HmC-2 and HmC-3 in two solvents  $\text{CH}_3\text{CN}$  and  $\text{CH}_2\text{Cl}_2$ , have also been investigated with of iodossylbenzene (PhIO) as terminal oxidant. The epoxidation study with HmC-1 as catalyst was reported earlier using PhIO as oxidant. Highly ordered 2D-hexagonal mesoporous silica has been functionalized with 3-aminopropyltriethoxysilane (3-APTES) and this has been used to heterogenize the three synthesized homogeneous catalysts and thereby obtained three new heterogeneous catalysts HtC-1, HtC-2 and HtC-3. The heterogeneous catalysts have been characterized by FT-IR, solid state UV-Vis spectroscopy, powder X-ray diffraction (XRD) and scanning electron microscopy (SEM). The catalytic activity of these heterogeneous catalysts [HtC-(1-3)] for epoxidation of alkenes has been investigated in the presence of two terminal oxidants PhIO and TBHP, in two solvents  $\text{CH}_3\text{CN}$  and  $\text{CH}_2\text{Cl}_2$  under mild conditions and compared their activity with their homogeneous counterpart.

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## 1. Introduction

Catalytic epoxidation of olefins is an important synthetic method for both industry and academics [1]. Both homogeneous as well as heterogeneous catalytic systems are in use for that purpose. Transition metal complexes of salen type ligands are the most widely used homogeneous catalysts for epoxidation of olefins [2–4]. Usually, the product yields in homogenous catalytic reactions are very high because all the catalytic active sites are accessible, but the difficulty in separation of the catalyst and reaction products limits their scope. Heterogeneous catalysts appear to be a solution to this issue [5–7], because they have various attractive features such as easy product separation and catalyst recovery. So the heterogenization of homogeneous catalysts constitutes an interesting research area [8–13]. Various types of heterogenized catalysts are the metal complexes immobilized into solid supports such as molecular sieves [9,10], ion-exchange resins [11], polymer membrane [12], zeolite [14], and organic nanotubes [15] etc. Such immobilization often lowers the reactivity of these catalytic systems than that of homogenous catalysts due to the lower availability of active sites during the catalytic reactions. For instance,

although a handful of heterogenized catalysts developed for epoxidation of unfunctionalized alkenes are in literature [16–23], most of them exhibit considerably lower activity [16–21] than their homogeneous counterparts. Beside this, heterogeneous catalysts sometime require high energy processes and drastic synthetic conditions for their preparation. So search for the new heterogenization method is crucial. Che et al. in 1999 reported [13] heterogenization of a homogeneous Cr(III)-Schiff-base catalyst via immobilizing on a modified MCM-41. They made co-ordinately unsaturated Cr(III)-Schiff-base complexes and took modified MCM-41 having terminal  $\text{NH}_2$  group on the surface. Heterogenization was done through coordination of the chromium ion to the terminal  $\text{NH}_2$  group of the surface-bound tether *via* simple addition or ligand substitution reactions. Recently Bhaumik et al. reported [24] another interesting way to produce immobilized Schiff-base ligand complexes of Ni(II) and Cu(II). They first of all functionalized highly ordered 2D-hexagonal mesoporous silica with 3-aminopropyltriethoxysilane (3-APTES) and then condensed it with a dialdehyde, 2,6-diformyl-4-methylphenol. The material thus obtained was separately treated with methanolic solution of copper(II) chloride and nickel(II) chloride to obtain copper and nickel anchored mesoporous materials, designated as Cu-AMM and Ni-AMM, respectively. However, the exact structures of the active sites of the heterogenized catalysts obtained following the above two methods seemed to be uncertain. In order to overcome

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that shortcoming here we introduce a new methodology to heterogenize homogenous catalysts. First of all we have synthesised Mn(III), Fe(III) and Co(III) complexes of a salen type ligand  $N,N'$ -ethylenebis(3-formyl-5-methylsalicylaldehyde) ( $L^1$ ) as homogeneous epoxidation catalyst where the salen ligand contains two uncoordinated formyl groups. Then heterogenization of these three structurally characterized homogeneous catalysts has been done following the steps as schematically represented in Scheme 1. The heterogenized catalysts thus obtained have been explored as epoxidation catalysts employing (*E*)-stilbene, styrene, cyclooctene and 1-octene as substrates in presence of *tert*-butyl hydrogen peroxide (TBHP) and PhIO as terminal oxidants in two solvents, acetonitrile and dichloromethane and their activities have been compared with their homogeneous counterpart. Here it is to note that syntheses of Mn complex and analogous complex of Fe with  $\text{ClO}_4^-$  as counter anion and some of their catalytic activity were reported earlier [25,26].

## 2. Experimental

### 2.1. Methods

Elemental analyses (carbon, hydrogen and nitrogen) were performed using a Perkin–Elmer 240 °C elemental analyzer. Infrared spectra ( $4000\text{--}500\text{ cm}^{-1}$ ) were recorded at 27 °C using a Perkin–Elmer RXI FT-IR spectrophotometer with KBr pellets. Electronic spectra ( $800\text{--}200\text{ nm}$ ) were obtained at 27 °C using a Shimadzu UV-3101PC with methanol as solvent and reference. The  $^1\text{H}$  NMR spectra were recorded on a Bruker AC300 spectrometer. Magnetic susceptibilities were measured at 27 °C using an EG and G PAR 155 vibrating sample magnetometer with  $\text{Hg}[\text{Co}(\text{SCN})_4]$  as reference; diamagnetic corrections were made using Pascal's constants. Thermal analyses (TG–DTA) were carried out on a Mettler Toledo (TGA/SDTA851) thermal analyzer in flowing dinitrogen (flow rate:  $30\text{ cm}^3\text{ min}^{-1}$ ). The electrospray mass spectra were recorded on a MICROMASS Q-TOF mass spectrometer. The cyclic voltammetric measurements were carried out in dry acetonitrile solutions with 0.2 M TBAP as supporting electrolyte (scan rate =  $10\text{ mV s}^{-1}$ ) employing a PAR potentiostat/galvanostat model Versa Stat-II. A three electrode system was used in which the counter and working electrodes were platinum foils and the reference electrode was a saturated calomel electrode. Field Emission Scanning Electron Microscope (FE-SEM) measurement was carried out with JEOL JSM-6700F field-emission microscope. X-ray powder diffraction (XRPD) was performed on a XPERT-PRO Diffractometer monochromated Cu  $K\alpha$  radiation (40.0 kV, 30.0 mA) at room temperature.

### 2.2. Materials

All chemicals were obtained from commercial sources and used as received. Solvents were dried according to standard procedure and distilled prior to use. Styrene, (*E*)-stilbene, cyclooctene, 1-octene, *tert*-butyl hydrogen peroxide (TBHP) were purchased from Aldrich and used in epoxidation experiments without further purification. Polyethylene glycol dodecyl ether (Brij-35), tetramethylammoniumhydroxide (TMAOH) were purchased from Aldrich. 3-aminopropyltriethoxysilane (3-APTES), cetyl trimethyl ammonium bromide (CTAB) were purchased from Spectrochem and Tartaric acid (TA) from Merck.

### 2.3. Preparation of the functionalized mesoporous material (M-II)

The functionalized mesoporous material (M-II) was prepared by following the reported method [27].

### 2.4. Synthesis of ligand ( $L^1$ ) and homogenous catalysts

2, 6-Diformyl-4-methylphenol was prepared according to the literature method [28]. The Schiff-base  $N,N'$ -ethylenebis(3-formyl-5-methylsalicylaldehyde) ( $L^1$ ) was synthesized following the similar procedure as we reported earlier [25].

### 2.5. Synthesis of homogenous catalysts (HmC)

#### 2.5.1. $\text{MnL}^1\text{Cl}\cdot 2\text{H}_2\text{O}$ (1.2 $\text{H}_2\text{O}$ ) (HmC-1)

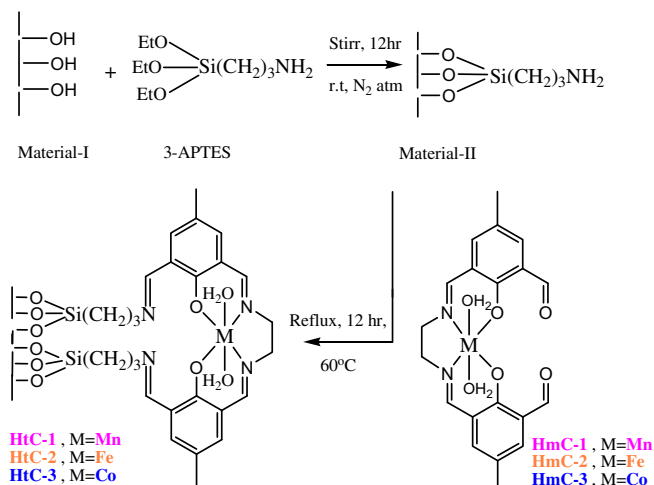
HmC-1 was synthesized and characterized according to same procedure as reported earlier [25].

#### 2.5.2. $\text{FeL}^1(\text{NO}_3)\cdot 3\text{H}_2\text{O}$ (HmC-2)

HmC-2 was synthesized by drop wise addition of an aqueous solution (20 mL) of  $\text{Fe}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$  (0.404 g, 1 mmol) to a heated suspension of  $L^1$  (0.352 g, 1 mmol) in ethanol (50 mL). A brown color developed immediately upon dissolution of the ligand. The solution was allowed to stir open to the atmosphere for 6 h. A clear deep brown solution was obtained. The solution was kept for crystallization. After a few days, brown crystals of HmC-2 (0.38 g, 75%) suitable for X-ray data collection were separated out. *Anal. Calc.* for  $\text{FeL}^1(\text{NO}_3)\cdot 3\text{H}_2\text{O}$ : C, 45.98; H, 4.59; N, 8.04. Found: C, 45.68; H, 4.60; N, 8.01%. IR (KBr):  $\nu(\text{C}=\text{O})$   $1656\text{ cm}^{-1}$ ;  $\nu(\text{C}=\text{N})$   $1622\text{ cm}^{-1}$ ;  $\nu(\text{skeletal vibration})$   $1544\text{ cm}^{-1}$ ;  $\nu(\text{H}_2\text{O})$   $3403\text{ cm}^{-1}$ ;  $\nu(\text{NO}_3^-)$   $1381$ . UV  $\lambda_{\text{max}}$  (MeOH)/nm 333, 501sh ( $\epsilon/\text{dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$  7100, 1137).

#### 2.5.3. $\text{CoL}^1(\text{NO}_3)\cdot 2\text{H}_2\text{O}$ (HmC-3)

HmC-3 was synthesized by drop wise addition of an aqueous solution (20 mL) of  $\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$  (0.291 g, 1 mmol) to a heated suspension of  $L^1$  (0.352 g, 1 mmol) in ethanol (50 mL). A reddish-brown color developed immediately upon dissolution of the ligand. The solution was allowed to stir open to the atmosphere for 6 h. A brown complex (0.41 g, 80%) thus precipitated was isolated by filtration, washed with water and dried in vacuum. *Anal. Calc.* for  $\text{CoL}^1(\text{NO}_3)\cdot 2\text{H}_2\text{O}$ : C, 47.33; H, 4.33; N, 8.28. Found: C, 47.32; H, 4.35; N, 8.30%. IR (KBr):  $\nu(\text{C}=\text{O})$   $1660.5\text{ cm}^{-1}$ ;  $\nu(\text{C}=\text{N})$   $1624.9\text{ cm}^{-1}$ ;  $\nu(\text{H}_2\text{O})$   $3330.8\text{ cm}^{-1}$ ;  $\nu(\text{skeletal vibration})$   $1546.9\text{ cm}^{-1}$ ;  $\nu(\text{NO}_3^-)$   $1384.5\text{ cm}^{-1}$ .  $^1\text{H}$  NMR (300 MHz,  $\text{D}_6\text{-DMSO}$ ):  $\delta$  11.09 (2H, s, Ar-CHO), 8.36 (2H, s, -CH=N-), 7.66 (4H, s, Ar-H), 4.18 (4H, s, N-CH<sub>2</sub>-CH<sub>2</sub>-N), 2.04 (6H, s, Ar-CH<sub>3</sub>). UV  $\lambda_{\text{max}}$  (MeOH)/nm 324, 410, 608sh ( $\epsilon/\text{dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$  22,000, 37500, 4000). TG analysis: 0.923 mg weight loss (7.22% of 12.77 mg complete: expected weight loss 7.1%) at 125 °C ESI-MS:  $m/z = 477.93\text{ amu}$  corresponds to  $[\text{CoL}^1\cdot 2\text{H}_2\text{O} + \text{MeOH}]^+$ .



Scheme 1. Synthetic out-line of the catalysts.

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