

Polymer Supported Schiff Base Iron Complex for Epoxidation of *Trans*-stilbene

N. Nath, H. C. Pradhan, T. Maharana, and A. K. Sutar

Abstract—In the present investigation, the novel recyclable polystyrene anchored iron complex supported by –ONN Schiff base is synthesized. This polymer anchored iron complex is prepared by the reactions of metal solution with one molar equivalent of polystyrene supported Schiff-base ligands in methanol under nitrogen atmosphere. In contrast with other polymer-supported catalysts, the greatest advantage of this catalyst system was that the cost of the catalyst was remarkably low and recycled up to six times, due to the easily accessible materials and the simple synthetic route. The higher efficiency of complexation of metal ions on the polymer anchored Schiff base than unsupported analogue was another advantages of this catalyst system. The structural study reveal that iron(III) complex is octahedral in geometry. The catalytic activities of polystyrene supported iron complex toward the epoxidation of *trans*-Stilbene is investigated. Experimental results indicate that the reactivity of iron complex is dramatically affected by the polymer support and the rate of *trans*-Stilbene conversion was 4.27×10^{-7} mole $\text{dm}^{-3}\text{s}^{-1}$ and obeys first order kinetics. The efficiency of supported catalysts remained almost constant upto six recycles.

Index Terms—Oxidation, polymers, catalysis, iron, *trans*-stilbene.

I. INTRODUCTION

Since the beginning of concept of Schiff base chemistry, it has been the constant challenge for scientists to search and find new Schiff base metal complexes [1] because of the wide applications in catalysis, oxygen storage devices [2] and also present antitumoral, antiviral, and antibacterial activity [3] and are used as mimetic systems for enzyme models. [4] Metal complexes of Schiff bases were used as catalyst for the organic transformations such as oxidation [5], [6], olefin epoxidation [7], [8], polymerization of ethylene [9] even though homogeneous catalysts suffer from drawback of poor catalyst recovery and product separation [10]-[12]. However, it was found that the homogeneous Schiff base catalytic systems have two major disadvantages: 1) the lack of control of product, which causes the reactor fouling and 2) the limitation of its use in solution process. In order to overcome to this limitation and combine the advantages of homogeneous and heterogeneous catalyst, homogeneous catalysts have been immobilized in several heterogeneous organic and inorganic supports [13], [14]. In addition to inorganic supports, polymeric supports have gained interest

because they are inert, nontoxic, nonvolatile, insoluble and recyclable [15], [16]. Among the polymeric supports, chloromethylated polystyrene crosslinked with divinylbenzene is one of the most widely used supports [17]. Recently, epoxidation of alkenes is one of the most widely studied reactions in organic chemistry, as the product epoxides, are used widely as intermediates in organic synthesis, pharmaceuticals as well as polymer production. They are used to provide industrially important products like surfactants, detergents, antistatic agents and corrosion protection agents, lubricating oils, textiles and cosmetics and it also play a key role in the formation of various biologically active compounds [18].

Epoxidation of stilbene using various chemical reagents such as, hydrogen peroxide, permanganate, molecular oxygen and ozone, are widely used [1]. The use of hydrogen peroxide has the advantage of producing oxygen and can be used to augment biological degradation [6]. Besides, the adoption of H_2O_2 as an alternative of current industrial oxidation processes offers environmental advantages, some of which are: a) replacement of stoichiometric metal oxidants; b) replacement of halogens; c) replacement or reduction of solvent usage; and d) avoidance of salt by-products. Hydrogen peroxide works either alone or with a catalyst. But with catalyst, it gives better results. Iron is the most common homogeneous catalyst for hydrogen peroxide [6].

This paper reports the synthesis and characterization of new polymer supported Schiff base complexes of iron(III) and their catalytic activity towards epoxidation of *trans*-Stilbene, using H_2O_2 as oxidant.

II. MATERIALS

Divinyl benzene cross-linked chloromethylated polystyrene beads (with chlorine content 2.5–4 mmol/g) was obtained from “Ion Exchange India Ltd.” (India). FeCl_3 , *trans*-Stilbene (purity 95.5%), H_2O_2 (30.0 wt %), ethylenediamine and 2-hydroxy -1-naphthaldehyde were procured from “Merck” (India). Other chemicals and solvents were of analytical grade (>99.0wt%).

Characterization of the Polymer Supported Schiff Base and Its Iron Complex

IR spectra of polymer supported Schiff base and its iron complexes were recorded on KBr pellet using Perkin-Elmer 1600 FTIR Spectrophotometer. The electronic spectra of Schiff base and its iron complexes were recorded with Shimadzu 1601 PC UV-Vis Spectrophotometer by using sample mull in a cuvette. Thermo gravimetric analysis (TGA) of Schiff base and its ion complex was carried out using Perkin-Elmer Pyris, Diamond Thermal Analyzer under

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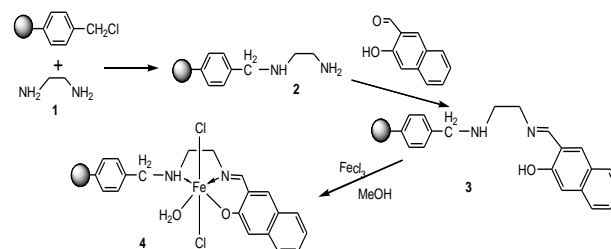
nitrogen atmosphere at a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$. The loading of iron ion on Schiff base was determined by analyzing the loading solution with Perkin-Elmer 3100 Atomic Absorption Spectrometer at λ_{max} of corresponding metal ions. The $^1\text{H-NMR}$ spectra of Schiff base and its metal complexes were recorded on an FT-NMR-Brucker 300 MHz Spectrometer using DMSO-d_6 as a solvent and tetramethylsilane (TMS) as an internal reference. The magnetic moment (μ) of metal complexes was measured using Vibrating Sample Magnetometer-155. The molecular weight of Schiff base was determined using a Vapor Pressure Osmometer (Merck VAPRO 5600, Germany).

III. RESULTS AND DISCUSSION

The oxidation of stilbene with polymer-anchored Schiff base complexes of iron ion was found to be higher and more selective than those with unsupported Schiff base complexes of this metal ion. These results clearly indicate that a polymer support plays a positive role in modifying the activity of metal-ion complexes, as reported in the literature [1]. The activity of a catalyst on a support is increased, provided that the nature of the catalyst is not destroyed and the support is able to provide a liquid-phase environment as found with polymer supports; hence, the properties of polymer supports influence the activity of anchored catalysts. Although the amount of loaded metal ions influences the activity of a supported catalyst, the activity of a supported catalyst is also influenced by leaching of the catalyst from the polymer support [1]. The leaching of catalysts from the polymer-anchored complexes was determined by an analysis of the recycled catalyst ash for loaded metal ions with an atomic absorption spectrometer, and it was found to be insignificant for polymer-supported catalysts recycled up to six times. The analysis of the recycled catalysts also indicated that the supported catalysts were stable and maintained their catalytic activity in the oxidation of phenol without leaching of metal ions as found with physically anchored catalysts [8]. The thermal stability of the supported Schiff base and iron catalysts was also analyzed for their applications in high-temperature reactions and to provide proof for the complexation of metal ions with a polymer-anchored Schiff base. The TGA of polymer supported Schiff base showed a weight loss of 40.4 wt% at $500\text{ }^{\circ}\text{C}$, but its iron(III) showed a weight loss of 25.2 at same temperature, which was clear indication that iron(III) ion complexes were more stable [7]. In addition to thermal analysis, the polymer-supported metal complexes of Schiff base were also characterized by IR and UV techniques to provide a proof for the complexation of metal ions and to decide the structures and geometries of metal complexes on the basis of elemental analysis and magnetic properties of metal complexes.

Excellent selectivity of epoxidation for *trans*-Stilbene was obtained. The immobilized polymer anchored catalysts can be reused for more than six times without any significant loss in their activities. The polymer supported Schiff base ligand(L) has been synthesized (Scheme 1) by refluxing 1 gm of chloromethylated poly(styrene-divinyl benzene) with ethylenediamine in THF at room temperature for 48h. The

white beads thus obtained were washed off with demonized water followed by methanol and dried in vacuum. Thus the dried beads were reacted with 2-hydroxy-1-naphthaldehyde in toluene and refluxed for 24 h. The product thus formed was washed with toluene followed by methanol and dried under vacuum. The FeL Schiff base complex was prepared by the reaction of FeCl_3 with L (Scheme 1).



Scheme 1. Preparation of polymer-anchored schiff base catalyst.

The FTIR spectra conforms the attachment of polymer support. The band at 1261cm^{-1} is due to the presence of C-Cl in pure chloro methylated polystyrene (1). The intensity of this C-Cl band decreased in the polymer supported metal complex, which is the clear indication of attachment of polymer support. The band at 3432cm^{-1} represent to N-H stretching (secondary amine) vibration of polymer-anchored ethylenediamine (2) and the band at 1629cm^{-1} due to N-H bending vibration of primary amine, which reduced in intensity when reacted with 2-Hydroxy-1-naphthaldehyde. The stretching vibration of azomethine group (C-N) at 1622cm^{-1} of polymer-anchored Schiff base ligand (3) was shifted to the lower frequency at 1610cm^{-1} in the iron complex (4). This gives the clear indication that Schiff base is attached to the iron through the azomethine nitrogen. The appearance of new absorption band at 414cm^{-1} and 544cm^{-1} in polymer-anchored Schiff base iron complex is due to the formation of Fe-N bond and Fe-O bond, respectively [19]. The magnetic moment (5.08 B.M) of iron complex indicates a high-spin octahedral geometry [20], [21]. The complex exhibit ligand to metal charge transfer(LMCT) transitions as well as low intensity spin forbidden d-d transition, as high-spin Fe(III) complex (d^5) is oxidizing in nature. The electronic spectrum also conform the structure. Three broad bands in the range 245–270nm, 318-343nm and 463-492nm were observed. And among these, the very low intensity bands at 463-492nm may be represent to $^6\text{A}_{1g} \rightarrow ^4\text{A}_{1g}(\text{G})$ and $^6\text{A}_{1g} \rightarrow ^4\text{T}_{2g}(\text{G})$ transitions in octahedral symmetry of Fe(III) complex [22], [23]. The intensities of the bands in the spectrum are affected possibly due to the low loading of the Fe(III) complex to polymer support. The catalytic activity of polymer-anchored Fe(III) Schiff base complex was tested in epoxidation of *trans*-Stilbene as a model substrate using different solvents at 50°C (Table I).

TABLE I: EPOXIDATION OF *TRANS*-STILBENE CATALYZED BY IRON COMPLEX 4^a

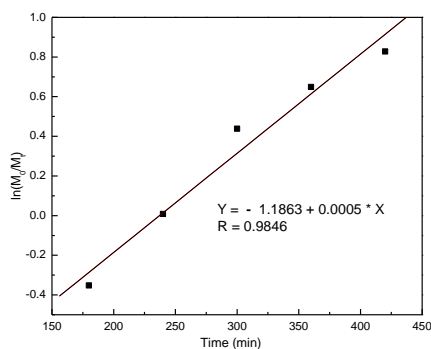
Solvent	Time(h)	Conversion (%)
CH_3CN	6.5	70
MeOH	6.5	54
CH_2Cl_2	6.5	50

^a Reaction conditions: (10mL) solvent, (5mmol) *trans*-Stilbene, (10mmol) oxidant(H_2O_2) and (0.05gm) catalyst.

TABLE II: EFFICIENCY OF RECYCLED SUPPORTED CATALYSTS IN EPOXIDATION OF *TRANS*-STILBENE

		Recycle number				
		0	2	4	6	8
Supported Iron Complex	Conversion	69.6	67.3	60.2	55.6	34.4
	Selectivity	89.9	90.3	88.2	86.2	81.9

trans-Stilbene=5mmol, oxidant(H₂O₂) =10mmol and catalyst =0.05gm, Temp. =50 °C. CH₃CN =10.0mL.

Fig. 1. Semilogarithmic plots of *trans*-Stilbene conversion in time.

This result shows that in presence of CH₃CN, higher epoxidation yield was observed as compared to MeOH and CH₂Cl₂. This is because the dielectric constant of CH₃CN ($\epsilon=37.5$) is high as compared to MeOH ($\epsilon=32.5$) and CH₂Cl₂ ($\epsilon=8.9$). This may be due to the polarity of solvent and the better solubility of the oxidant and substrate in the solvent [19]. The polymer support has facilitated the decomposition of intermediates; hence, % conversion of *trans*-Stilbene was more with polymer-supported metal complexes in comparison to free iron complex. The conversion of *trans*-Stilbene by iron catalyst was high at 300 min and then after the conversion became almost constant due to substantial decrease in the concentration of oxidant and substrate in the reaction mixture. The amount of *trans*-Stilbene oxidized with H₂O₂ was almost equal to the sum of amount of *trans*-Stilbene epoxide and benzaldehyde produced, which indicates the formation of other reaction products are almost none. However, the reaction showed high selectivity for *trans*-Stilbene epoxide as determined from the area under the GC-chromatograms. The supported catalyst was recycled and also further evaluated for their catalytic activity after their applications in epoxidation reaction. The efficiency of supported catalysts remained almost constant upto six recycles and further there is significant decrease (Table II) which may be due to either decomposition of the catalyst in the reaction media or their extraction to the organic solvent during product isolation. [24] The product selectivity for epoxide remained unaffected on using recycled catalysts, which was an indication for the structural stability of iron complex on polymer support as confirmed by comparing IR spectra of recycled catalysts with IR spectra of freshly prepared catalysts. The rate of *trans*-Stilbene conversion was 4.27×10^{-7} mole dm⁻³ s⁻¹ in the presence of polymer-supported iron Schiff base complex. We have performed kinetic studies for the *trans*-Stilbene epoxidation using iron catalyst in the presence of H₂O₂. The results are depicted in Fig. 1. This plot (Fig. 1) implies that the epoxidation reaction obeys first order kinetics. There is

complete absence of induction period. The $\ln[M]_0/[M]_t$ vs time plots is linear. The values of the apparent rate constant (k_{app}) may be calculated from the slope of these plots. The value of k_{app} for *trans*-Stilbene epoxidation in the presence of H₂O₂ was found to be 0.0005 h⁻¹. It was also observed that when oxidant was changed to TBHP, the conversion was low (63%) at the same condition. This may be due to immiscible character TBHP in comparison to H₂O₂ with the substrate.

IV. CONCLUSIONS

The simple preparation procedure for polymer anchored Fe Schiff base complex on polystyrene support has been reported. The catalytic activity towards epoxidation of *trans*-Stilbene has been tested for complex 4 and found highly active and selective catalyst. The epoxidation of *trans*-Stilbene showed high selectivity for epoxide formation. The complex 4 is reusable since it withstand up to six recycling without any loss in their activity.

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