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## RESEARCH ARTICLE

### PS-DVB SUPPORTED SCHIFF BASE COBALT (II)-AS AN EFFICIENT HETEROGENEOUS CATALYST SYSTEM FOR KNOEVENAGEL REACTION

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#### ABSTRACT

This work focuses on synthesis, characterization and catalytic activity study of PS-DVB supported Schiff base cobalt complex. It is synthesized by reaction between aminated DVB cross linked polystyrene and cobalt chloride solution and stabilized by Schiff base. The prepared catalyst was characterized by FT-IR and the surface morphological analysis studies were carried out by using SEM. The catalytic activity and efficiency of the catalyst was studied by using Knoevenagel reaction.

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## INTRODUCTION

Catalysis is the increase in the rate of a chemical reaction due to the participation of an additional substance called a catalyst. In the catalyzed mechanisms they usually react to form a temporary intermediate which then regenerates the original catalyst in a cyclic process (Gupta, 2002). The catalytic support can be provided with the help of the cross linked PS-DVB because of their properties such as nontoxicity, inertness, higher thermal stability and recycling property (Nicholas, 2002). The product can be separated easily from the catalyst and it offers more practical flexibility (Hine, 1967). When compared with heterogeneous and homogeneous catalyst, the metal complex is having greater catalytic property (Garnovskil, 1996; Yousaf, 2013). It is the presence of Cobalt complex that give the organic PS-DVB an inorganic environment and functionality (Anupama, 2013). A wide variety of investigations have been carried out on PS-DVB metal complex; these include studies of thermal conductivity, thermodynamic stability, redox reactions, collection of metal ions biomedical effects etc (Fessenden, 1998). The concentration of reactants on the active site can be controlled by Cross linked PS-DVB, and hence they are more efficient on

controlling the activity of the metal complex (Khalid, 2012; Khalid, 2012). Here Schiff base is used for the stabilization of PS-DVB Cobalt complex. Schiff base derived from aromatic and aliphatic aldehydes have a wide variety of applications in many fields, e.g., biological, inorganic and analytical chemistry (Anaconda, 1999; Trujillo, 2008). Transition metal complexes with Schiff bases have expanded enormously and embraced wide and diversified subjects comprising vast areas of organometallic compounds and various aspects of biocoordination chemistry (Valcarcel, 1994). Metal complexes of Schiff base have great interest due to their preparative accessibility, structural variability and tunable electronic properties (Yousaf, 2011). Schiff bases are used in optical and electrochemical sensors as well as in various chromatographic methods (Lawrence, 1976; Patai, 1970). The transition metal complexes are widely used as catalyst for many of the reactions like epoxidation, isomerisation, hydrogenation, oxidation etc. Because of the higher thermal and moisture stability the PS-DVB supported Schiff base metal complexes are having higher activity in the reactions involving higher temperature (Spichiger, 1998). Cobalt is particularly selected because of its features like oxidation and reduction property, due to greater stability to form complex, capacity to form more than one ion in solution phase, cheap and it is relatively abundant which makes suitable for industrial application (Clarke, 1998). The Knoevenagel condensation reaction is one of the most industrially important reactions that involve the

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formation of C=C during the organic synthesis here, an aldehyde or a ketone and an activated methylene is converted to a substituted olefin by using amine as catalyst.

## MATERIALS AND METHODS

Chemicals like Polystyrene, Divinyl benzene, tin chloride,  $H_2SO_4$  and  $HNO_3$  were provided by Sigma Aldrich Company and they were used as supplied. All metal (II) salts were used as chlorides. The FTIR spectra were recorded on a Bruker IFS-55 spectrometer using KBr pellets. The scanning electron micrographs were taken using a Hitachi S-2400 instrument.

**Synthesis of DVB cross linked polystyrene:** Free radical suspension Polymerization is used for the synthesis of cross linked polystyrene. For the synthesis of 2% DVB Cross linked polystyrene, a mixture of styrene (98mmol), DVB (2mmol), toluene (8ml), benzyl peroxide (1g) was prepared. It is then suspended in 1% PVA solution. The above mixture is mechanically stirred at  $80^\circ C$ . polymerization was completed after 6 hours. The beaded product is collected by filtration washed with acetone and methanol (Lawrence, 1976)

**Nitration of DVB cross linked polystyrene:** About 5g of DVB cross linked polystyrene was nitrated with 5:2 mixture of sulphuric acid and nitric acid at  $60^\circ C$  on a controlled water bath for 1hr. The resulting derivative is diluted with water and washed repeatedly with distilled water till free from acid. (15)

**Reduction to amino derivative:** With a mixture of tin chloride (40g), concentrated HCl (45ml) in 50 ml ethanol for 12hr at  $90^\circ C$  under nitrogen atmosphere. The product was filtered, washed first with distilled water and then with 2M NaOH to recover the free amino PS-DVB.

**Metal binding:** The poly amino styrene was prepared and stirred with excess aqueous solution of metal chloride for 12hr and then washed with water.

**Stabilization of metal PS-DVB-amino complex:** The metal loaded poly 4 amino styrene is reacted with .2M solution of Schiff base ligands in dichloromethane (DCM) to get the immobilized metal complex (Spichiger, 1998).

**Preparation of Schiff base:** 10 milli moles of ethylene diamine and 10 milimoles of salicylaldehyde are mixed together with constant stirring, Schiff base will get precipitated and it is dissolved in the dichloromethane.

**Application in Knoevenagel reaction:** The Knoevenagel condensation is an organic reaction used to convert an aldehyde or ketone and an activated ethylene to a substituted olefin using an amine base as a catalyst. The reaction begins by deprotonation of the activated methylene by the base to give a resonance stabilized enolate. The amine catalyst also reacts with the aldehyde or ketone to form an iminium ion intermediate, which then gets attacked by the enolate. The intermediate compound formed gets deprotonated by the base to give another enolate while the amine of the intermediate gets protonated. A rearrangement then ensues which releases the amine base, regenerates the catalyst, and yields the final olefin product.

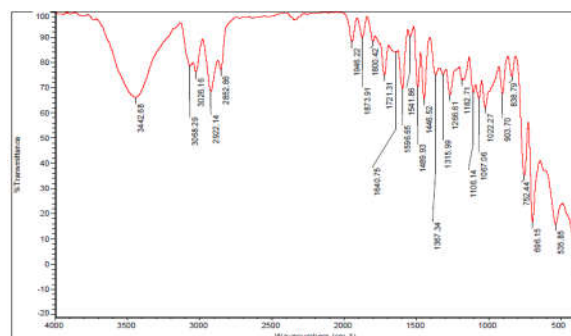
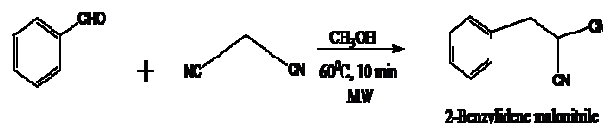


Fig. 1. IR Spectra of PS-DVB

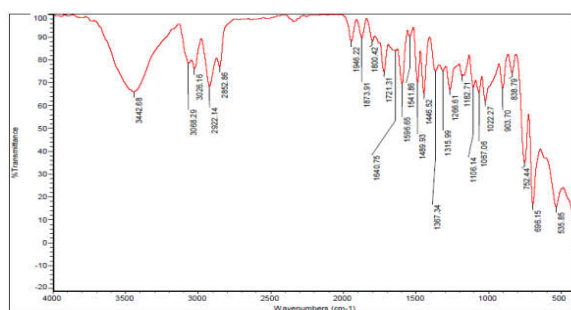


Fig 2. IR Spectra of aminated PS-DVB.

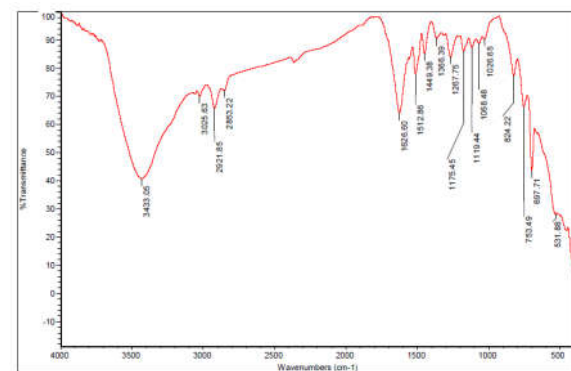


Fig. 3. IR Spectra of PS-DVB Co (II)

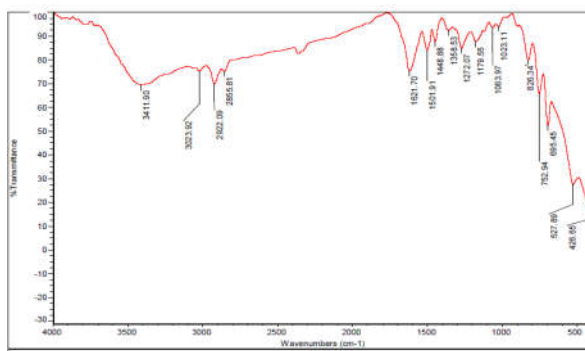


Fig. 4. IR Spectra of PS-DVB Schiff base Co (II).

5 milli moles of benzaldehyde and 5 milli moles of malanonitrile are mixed together along with the Schiff base PS-DVB metal complex.

The product formed is 2-Benzylidene malonitrile and formation takes place within the fraction of seconds. The product is dissolved in the methanol and filtered and the heterogeneous catalyst is recovered and the methanol is evaporated in the water bath and yield is noted.

## RESULTS AND DISCUSSION

The band at  $3436.11\text{cm}^{-1}$  (fig 2) indicates the N-H stretching of aminated DVB Cross linked Polystyrene. The band shift to lower frequency by  $3-25\text{cm}^{-1}$  (fig 3, 4) in the metal complexes indicates the coordination through the N atom. The N-H bending frequency increases from the aminated DVB Cross linked polystyrene due to the coordination with the metal and Schiff base. Metal-ligand peak appears at  $401.14\text{cm}^{-1}$  (fig 3) and it is further strengthened to  $426.65\text{cm}^{-1}$  (fig 4) due to the stabilization by Schiff base.

## SEM

The PS-DVB is having very smooth surface (fig. 5). The amination of PS-DVB introduces some irregularities which suggest the attachment of amine group on the surface (fig. 6). In the SEM image of aminated PS-DVB Co (II) the surface appears to be more roughened which indicates metal coordination (Fig. 7). The stabilization with Schiff base further changes the surface morphology by making a uniform distribution of Schiff base layer over it, having a tree like attachments and thus the coordination of metal is completed.

**Catalytic efficiency study:** The catalytic efficiency study was conducted by using 1mmoles of vanillin and Malonitrile by using methanol as reaction medium with 0.05g of catalyst. The efficiency was observed as 100% during the first cycle. The catalyst recovered from the first cycle was again made to react

Table 1. Vanillin in Methanol

	Vanillin (mmoles)	Malonitrile (mmoles)	Catalyst (gram)	Product (mmoles)	Efficiency
First cycle	1	1	0.05	0.00091	100%
Second cycle	1	1	0.05	0.00081	81%
Third cycle	1	1	0.05	0.00060	60.5%

Table 2. 3-hydroxybenzaldehyde in methanol

No	3-hydroxybenzaldehyde (mmoles)	Malonitrile (mmoles)	Catalyst (gram)	Efficiency (%)
First cycle	5	5	0.05	77.2
Second cycle	5	5	0.05	72.4
Third cycle	5	5	0.05	70.2

Table 3. 4-hydroxybenzaldehyde in methanol

No	4-hydroxybenzaldehyde (mmoles)	Malonitrile (mmoles)	Catalyst(gram)	Efficiency (%)
First cycle	5	5	0.05	80.6
Second cycle	5	5	0.05	73.6
Third cycle	5	5	0.05	71.4

The product yield is greater in the case of 4-hydroxybenzaldehyde, than 3-hydroxybenzaldehyde.

Table 4. Solvent effect

No	4-Hydroxybenzaldehyde (mmoles)	Malonitrile (mmoles)	Solvent	Catalyst(gram)	Efficiency (%)
1.	5	5	Methanol	0.05	80.6
2.	5	5	THF	0.05	69
3.	5	5	Chloroform	0.05	51.24

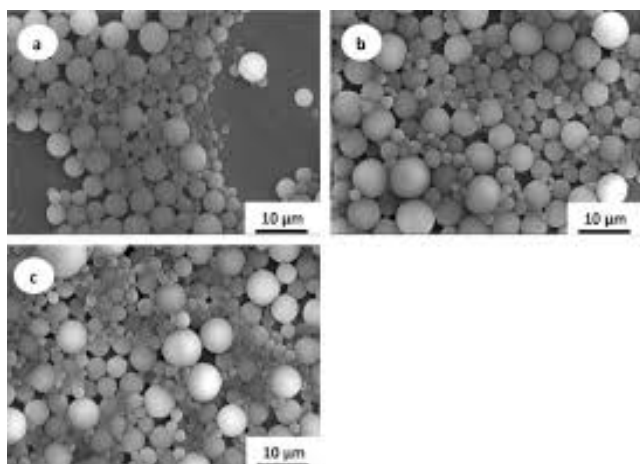


Fig. 5. SEM analysis of PS-DVB

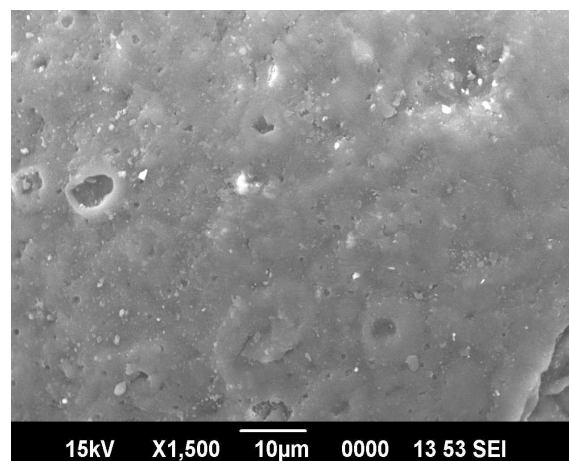


Fig. 6. SEM Analysis of aminated PS-DVB

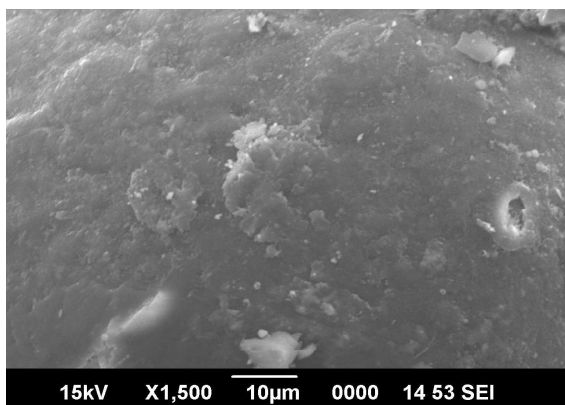


Fig. 7. SEM Analysis of PS-DVB Schiff base Co (II)

during the second cycle to obtain 81% efficiency followed by 60.5% efficiency on the third cycle. The product is greater in the case of methanol compared to chloroform and THF. As the polarity of solvent increases, the yield of product also increases.

### Conclusion

We have synthesized PS-DVB supported Schiff base Cobalt (II) and studied its catalytic activity particularly on Knoevenagel reaction. Conducted different cycle of experiment by using the recycled catalyst suggests that, it is an efficient catalyst and the same experiment is repeated for different aldehydes like vanillin, 3-hydroxybenzaldehyde and 4-hydroxybenzaldehyde. The product yield is greater in the case of 4-hydroxybenzaldehyde than 3-hydroxybenzaldehyde since the presence of electron donating group on the Para position increases electron density more on the reactant which further facilitates greater yield. Solvent effect studies are also conducted with different solvents like methanol, chloroform and THF. The product is greater in the case of methanol compared to chloroform and THF. As the polarity of solvent increases, the product yield also increases. Thus it is concluded that PS-DVB supported Schiff base cobalt (II) is an efficient heterogeneous catalyst system for Knoevenagel reaction.

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**Conflict of interest:** The authors declare that there is no conflict of interest regarding the publication of this paper.

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