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# Study of Catalytic Activity of Silica Supported Schiff Base Complexes

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The catalytic activity of silica supported Schiff base metal complexes have been studied for the oxidation of benzyl alcohol, using hydrogen peroxide, which gave benzaldehyde as a major product. Silica supported Schiff base complexes gave better results compared to unsupported Schiff base complexes. Schiff base metal complexes such as Cr(VI), Mo(VI) and W(VI) have played significant role to enhance their conversion and selectivity. Among these Cr(VI) showed better conversion.

**Keywords: Benzyl alcohol, Hydrogen peroxide, Oxidation, Schiff base metal complex.**

## INTRODUCTION

Schiff bases are most widely used in synthesis of organic compounds. They are used as pigments and dyes, catalysts, intermediates in organic synthesis and as polymer stabilizers [1]. Schiff bases are the important compound owing to their wide range of biological activities and industrial application. The oxidation of organic compounds is widely used reaction in laboratory scale for organic synthesis. The Schiff base transition metal complexes are a family of attractive oxidation catalysts for a variety of organic substrates because of their chemical and thermal stability. Therefore oxidation of benzyl alcohol to benzaldehyde is an industrially important reaction. Benzaldehyde is a versatile chemical intermediate widely used in the manufacture of pharmaceuticals, perfume and flavouring chemicals [2].

These types of Schiff base metal complexes have been explored in recent years for development in synthetic applications. Many of them are centered on the catalytic activity of Schiff base complexes in a large number of homogeneous and heterogeneous reactions.

Several research groups have developed different catalytic methods for oxidation of benzyl alcohol to benzaldehyde. However, only few references with useful heterogeneous catalysts for oxidation procedures have been reported [3,4]. Jacobsen *et al.* [5] reported that the chromium Schiff base metal complex were used as a catalyst for highly diastereoselective and enantioselective hetero Diels alder reaction and hetero ene reaction. Venkatramanan *et al.* [6] synthesized metal Schiff complexes and used as efficient catalysts for the oxygenation of heteroatom containing organic compounds with synthetic and mechanistic aspects. The Schiff base metal complexes found widespread use as efficient catalyst for the selective oxygenation of organic sulfides, sulfoxides and aromatic amines. The active oxidant can be generated from the complex using PhIO, $H_2O_2$, tBuOOH and $ClO^-$ as the oxygen source.

Catalytic asymmetric epoxidation of unfunctionalized olefins using silica, LDH (lactate dehydrogenase) and resin supported sulfonate –Mn (salen) complex were reported by Choudary and co-workers [7]. Variety of reactions such as asymmetric addition, epoxidation and oxidation on Schiff base supported catalyst as well as homogeneous catalyst were carried out on different substrates with good yield and as an efficient and recyclable catalyst [8-10]. A significant effort made towards the development of new catalyst for the synthesis of epoxide in a more environmental friendly way. Cobalt(II), Fe(III) and Ru(III) complexes of Schiff bases derived from hydroxy benzaldehyde were used in oxidation of cyclohexane into cyclohexanol and cyclohexanone in presence of hydrogen peroxide [11].

Binucleating complexes of various transition metals Fe, Co, Ni, Zn with Schiff bases acts as catalysts in the oligomerization of olefins [12]. Among these reported Schiff base cobalt(II) complexes catalysts were known to bind dioxygen more or less reversibly and therefore frequently studied as model compounds for natural oxygen carrier and for their use in $O_2$ storage, as well as in organic syntheses due to their catalytic properties under mild conditions [13,14]. Copper(II) complex with a tridentate imine, was revealed an efficient catalyst for oxidation of phenol, cyclohexene, styrene and benzyl alcohol using hydrogen peroxide and *tert*-butyl hydroperoxide as oxidant in homogeneous reaction [15-17]. Also catalytic activities of Schiff base aqua complexes of copper(II) towards hydrolysis of amino acid and esters were reported [18]. Priyarega *et al.* [19] were studied the catalytic oxidation property of ruthenium(III) complexes were also investigated for oxidation of benzyl alcohol, 1-phenylethanol and cyclohexanol by using $H_2O_2$, $O_2$, air, or *t*-BuOOH as oxidant. All these synthesized complexes were found to catalyze the oxidation of alcohol to carbonyl compound [20,21].

Herein we reported the simple method for the preparation of heterogeneous Schiff base catalyst consisting metal complexes heterogenized on silica matrix. The prepared material was tested as a catalyst on oxidation of benzyl alcohol to benzaldehyde and benzoic acid showed higher conversion of benzyl alcohol and also selectivity for benzaldehyde.

## EXPERIMENTAL

Ethyl alcohol, methyl alcohol, tetraethyl orthosilicate (TEOS), HCl and hydrogen peroxide (30 %) were obtained from Merck and were used without further purification.

The analyses of various liquid products obtained in the catalytic oxidation reactions were carried out by Shimadzu gas chromatography (GC 2014) having FID detector, a capillary column, with a programmed oven temperature from 50 to 200 °C and a 0.5 $cm^3$ $min^{-1}$ low rate of $N_2$ as a carrier gas.

**Preparation of silica composites:** One mole tetraethyl orthosilicate was mixed with 4 mol of ethanol, 4 mol of distilled water and stirred for 0.5 h, 0.01 M hydrochloric acid (HCl, 37 wt % in water) was added into the solution and then the solution was stirred at room temperature for 1 h and dried at 180 °C for 2 h.

**Preparation of heterogenized Schiff base complex catalyst:** Silica composite was activated by refluxing in concentrated hydrochloric acid and then washed thoroughly with deionized water and dried before undergoing chemical surface modification. Hydrated silica was then added to already prepared [22] and well characterized Schiff base complex solution (1 g in 10 mL of DMSO, 10 % catalyst) and the mixture was stirred over night. The solvent was removed by water bath at 70 °C. The resulting product was washed with alcohol and water until the colourless filtrate obtained. Further drying of solid product was carried out in an oven at 80 °C for 8 h. Similarly 5 % and 20 % silica supported Schiff base catalyst were prepared.

**Catalytic reaction on silica based ligand and Schiff base metal complexes:** Oxidation of alcohol was performed at various parameters in presence of catalyst with hydrogen peroxide as an oxidant. To the catalyst (0.2 g, 10 % catalysts), the substrate benzyl alcohol (1 mmol) was added and then hydrogen peroxide (10 mmol, 30 %) was added drop wise with continuous stirring. Reaction mixture was stirred until the TLC pointed out the reaction was completed. Reaction mixture was also analyzed by using gas chromatography.

Reaction was studied at different parameters such as effect of temperature, effect of various Schiff base catalysts, effect of molar ratio, effect of catalyst, effect of oxidizing agent and reuse of catalyst.

## RESULTS AND DISCUSSION

**Effect of temperatures on conversion of benzyl alcohol:** As the temperature increased from room temperature to 140 °C, the conversion increases but above 140 °C it start decreasing with formation of byproducts and other unidentified product in traces. The results of oxidation of benzyl alcohol with silica supported chromium Schiff base complex using hydrogen peroxide (30 %) as an oxidant at various temperatures were shown in Table-1. It showed that at 140 °C the conversion and selectivity were higher with no other by products, but at lower temperature it showed low conversion. The reaction could not take place at room temperature. The optimum temperature for benzyl alcohol oxidation with hydrogen peroxide catalyzed by silica supported Schiff base complexes was 140 °C.

TABLE-1
EFFECT OF TEMPERATURE ON
CONVERSION OF BENZYL ALCOHOL

| Temperature (°C) | Conversion of benzyl alcohol (%) | Selectivity of benzaldehyde (%) |
|---|---|---|
| Room temperature | No reaction | – |
| 60 | 6.81 | 99.98 |
| 80 | 14.18 | 95.42 |
| 120 | 27.50 | 82.00 |
| 140 | 32.16 | 94.00 |

Reaction conditions: benzyl alcohol = 1 mmol, catalyst = 0.25 g, 30 % $H_2O_2$ = 10 mmol, reaction time = 4 h

**Effect of various Schiff base catalyst:** The oxidation of benzyl alcohol was carried out to test the catalytic efficiency of the prepared Schiff base catalyst. An important advantage of this method that work up of reaction can done by simple filtration as it is heterogeneous catalyst.

In oxidation reaction of benzyl alcohol, silica supported ligand used as catalyst, which gave the lower conversion of benzyl alcohol with benzoic acid as major product and benzaldehyde as minor product, while reaction with supported metal complexes as catalyst gave benzaldehyde as major product. The supported Schiff base metal complexes showed higher catalytic activity than the supported ligand. In the absence of catalyst, no significant amount of benzaldehyde and benzoic acid was produced indicating that hydrogen peroxide alone is not sufficient to oxidize benzyl alcohol to benzaldehyde. Unsupported Cr-Schiff base complex gave lower conversion with difficult work-up of the reaction and more formation of byproducts as complex may get decompose. The results are shown in Table-2.

The conversion of the benzyl alcohol with silica supported chromium Schiff base complex showed 38.16 % and selectivity for benzaldehyde was 94 %, higher than other catalysts. These results indicated that among all the Schiff base catalyst, silica supported chromium Schiff base catalyst was an effective catalyst for oxidation of benzyl alcohol. The activity of Schiff base complexes of these transition metals showed significant improvements on their immobilization on silica support.

TABLE-2
OXIDATION OF BENZYL ALCOHOL USING HETEROGENIZED SILICA BASED SCHIFF BASE CATALYSTS

| Catalyst | Conversion of benzyl alcohol (%) | Selectivity of benzaldehyde (%) | Selectivity of Bz acid (%) |
|---|---|---|---|
| Unsupported Cr-Schiff base complex* | 15.50 | 20.50 | 35.50 (44-others) |
| Silica supported Ligand | 7.68 | 39.46 | 60.54 |
| Silica supported Mo–Schiff base complex | 28.48 | 88.69 | 11.31 |
| Silica supported Cr–Schiff base complex | 38.16 | 94.00 | 06.00 |
| Silica supported W–Schiff base complex | 19.08 | 82.00 | 18.00 |

Reaction conditions: benzyl alcohol = 1 mmol, catalyst-0.2 g, 30 % $H_2O_2$ = 10 mmol, temp. = 140 °C, reaction time = 4 h.
*Work-up difficult, homogeneous reaction.

**Effect of molar ratio:** To determine the effect of $H_2O_2$ (30 %) on the oxidation of benzyl alcohol, benzyl alcohol to $H_2O_2$ molar ratio varied from 1:10 and 1:20 mmol and other parameters kept constant such as catalyst, temperature and reaction time. The results were shown below in the form of bar diagram. A benzyl alcohol to $H_2O_2$ molar ratio of 1:10 resulted with conversion 38.16 %, with increase in selectivity of benzaldehyde and when benzyl alcohol to $H_2O_2$ molar ratio was changed to 1:20, conversion increased to nearly 47.76 %, but selectivity of benzaldehyde deceases (Fig. 1). This indicated that as the concentration of $H_2O_2$ increases, it oxidizes benzyl alcohol to higher selectivity for benzoic acid and less selectivity for benzaldehyde.

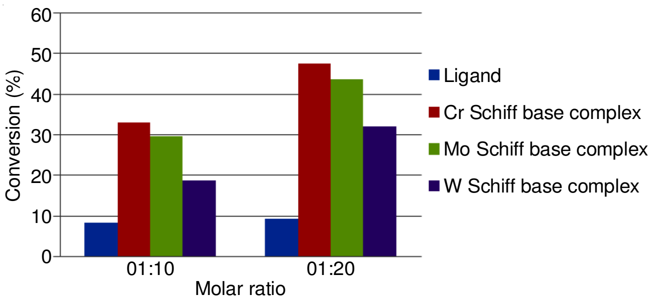

Fig. 1. Effect of molar ratio

**Effect of catalyst amount:** Oxidation of benzyl alcohol to benzaldehyde was carried out by using various amounts of catalyst using $H_2O_2$ as oxidant and results are presented in Table-3.

TABLE-3
EFFECT OF AMOUNT OF SILICA SUPPORTED
SCHIFF BASE CATALYST ON OXIDATION

| Amount of catalyst | Conversion of benzyl alcohol (%) | Selectivity of benzaldehyde (%) |
|---|---|---|
| Without catalyst | 10.86 | 52.80 |
| 0.2 g | 38.16 | 94.00 |
| 0.4 g | 14.58 | 85.23 |

Reaction conditions: benzyl alcohol = 1 mmol, 30 % $H_2O_2$ = 10 mmol, temp. = 140 °C, reaction time = 4h

Oxidation of benzyl alcohol was carried over various amounts of silica based chromium Schiff base complexes with molar ratio was 1:10 mmol of benzyl alcohol to aqueous $H_2O_2$ at 140 °C. The effect of amount of catalyst was studied over silica based chromium Schiff base complex catalyst which increases conversion of benzyl alcohol. The selectivity of benzaldehyde also depends upon the amount of catalyst used in catalytic reaction. The maximum conversion was 38.16 % with 0.2 g of catalyst. As the amount of catalyst was increased the conversion of benzyl alcohol decreases, selectivity was also decreased. It is concluded that the best result of oxidation of benzyl alcohol was obtained with 0.2 g of catalyst.

On the other hand, in the presence heterogeneous Schiff base catalyst the catalytic performance for the reaction was effectively improved. When Schiff base metal complex was used as catalyst in homogenous reaction, benzyl alcohol conversion increased but selectivity is decrease and also it showed formation of bi-products. It is reported in literature, the use of Schiff base metal complexes as catalyst in homogenous solution suffers from deactivation due to easy formation of dimeric peroxo and μ-oxo species.

**Effect of oxidizing agent:** The oxidation of benzyl alcohol was carried out at different oxidizing agents such as $H_2O_2$ and sodium per carbonate. In oxidation reaction of benzyl alcohol, sodium per carbonate using oxidising agent conversion was very low. The maximum product conversion 38.16 % was carried by using $H_2O_2$, chromium Schiff base complex catalyst (Table-4). The effect of oxidizing agent was studied of oxidation of benzyl alcohol.

TABLE-4
EFFECT OF OXIDISING AGENT ON
OXIDATION OF BENZYL ALCOHOL

| Oxidising agent | Conversion of benzyl alcohol (%) | Selectivity of benzaldehyde (%) |
|---|---|---|
| $H_2O_2$ | 38.16 | 94.00 |
| Sodium per carbonate | 4.38 | 67.80 |

Reaction condition: benzyl alcohol: $H_2O_2$ (1:10), catalyst-0.2 g, temperature-140 °C, time 4 h.

The stability of supported catalyst was monitored using multiple sequential oxidation of benzyl alcohol with hydrogen peroxide. An efficient catalytic oxidation procedure that allows the transformation of simple alcohol onto carbonyl compounds has been described in this study.

**Effect of amount of Schiff base metal complex loading on silica:** To study the best catalyst, different amount of chromium Schiff base complex on silica were loaded and catalytic activity was tested on benzyl alcohol oxidation. Oxidation of benzyl alcohol was carried with 5, 10 and 20 % catalysts which showed that the 10 % catalyst gave higher conversion (38.16 %) compared to other catalysts. It indicated that sufficient active sites required for the oxidation reaction with 10 % loading catalyst. So for further study silica supported (10 %) chromium Schiff base catalyst was used (Table-5).

The oxidation reaction of benzyl alcohol to benzaldehyde and benzoic acid was carried out at different loading of

TABLE-5
EFFECT OF LOADING METAL COMPLEXES ON SILICA SURFACE

| Loading of metal complex (%) | Conversion of benzyl alcohol (%) | Selectivity for benzaldehyde (%) |
|---|---|---|
| 1 | 23.10 | 80.20 |
| 5 | 27.66 | 86.09 |
| 10 | 38.16 | 94.00 |

chromium metal complex on silica supported catalyst such as 1-15 % loading. The amount of chromium loading on silica catalyst increased the conversion of benzyl alcohol and selectivity of benzaldehyde was also increased. At 10 % Cr-Schiff base complex supported on $SiO_2$ catalyst gave maximum conversion. But at 15 % Cr-Schiff base complex supported on $SiO_2$ catalyst loading of chromium was increased then selectivity as well as conversion was decreased.

## Conclusion

The prepared and well characterized Schiff base complexes systematically impregnated on silica and investigated for their performance as catalysts in the oxidation of benzyl alcohol to benzaldehyde and benzoic acid using $H_2O_2$ as oxidant. Catalytic activity of the complex indicated that chromium Schiff base complex gave maximum conversion, was carried out by changing the different parameter like reaction time, reaction temperature and amount of oxidant. Further research and developments in the area of Schiff base complexes transition metal ions would be highly useful to industries and academia.

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