

# Nanostructured Manganese Hexacyanidocobaltate(III) as Heterogeneous Catalyst for Solvent-Free Oxidation of Benzyl Alcohol

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**Abstract:** Manganese hexacyanidocobaltate(III) nanostructures have been synthesized using double decomposition method and characterized in terms of CHNS analysis, atomic absorption spectroscopy, thermal analysis, infrared spectral studies and transmission electron microscopic technique. The transmission electron microscopic image of the synthesized material showed that it is consisting of roughly spherical shaped particle with size range of 30-60 nm. The catalytic activity of the synthesized material was studied for the oxidation of benzyl alcohol, using H<sub>2</sub>O<sub>2</sub> as oxidant, under solvent-free conditions. The characterization of the oxidation product of benzyl alcohol and its quantitative estimation was done using gas chromatography. The synthesized material was found to be an effective heterogeneous catalyst with a high selectivity towards benzaldehyde as the oxidation product. It showed 31% conversion of benzyl alcohol under the optimized conditions of various reaction parameters, namely, amount of catalyst, reaction temperature, benzyl alcohol to H<sub>2</sub>O<sub>2</sub> molar ratio and the reaction time.

**Keywords:** Manganese hexacyanidocobaltate(III), Heterogeneous catalyst, Benzyl alcohol, Benzaldehyde.

## 1. INTRODUCTION

Transition metal hexacyanidometallates constitute a class of important coordination complexes which exhibit several distinctive properties such as water insolubility, mixed valency, high ionic conductivity and excellent redox mediator property [1-3]. A number of Prussian blue analogue complexes have been found to have polynuclear, microporous and open channel structure [4,5]. These materials remain undissolved upon their oxidation/reduction as their zeolitic structure easily permits the diffusion of ion inside or outside maintaining the electrical neutrality [6]. Due to these physico-chemical features, several transition metal hexacyanidoferrates have been utilized in designing of electrochromic device, molecular magnet, optical device, rechargeable solid state battery, ion-exchanger and adsorbent [7, 8]. Transition metal hexacyanidoferrates have been employed in the development of electroanalytical techniques for a wide range of molecules of environmental and biological importance. Several sensors based on transition metal hexacyanidoferrate have been prepared for electrochemical analysis of glucose, ascorbic acid, dopamine, epinephrine, norepinephrine,  $\beta$ -NADPH, insulin, morphine, paracetamol drug, hydrazine, thiosulfate, nitrate, phosphate etc. [9-16]. Also, few transition metal hexacyanidoferrates have been used as catalyst for commercially important polymerization reactions such as polymerization of ethylene oxide,

manufacturing of polyether polyols and copolymerization of carbon dioxide with propylene oxide [17-20]. Recently, the different applications of metal hexacyanidoferrate nanoparticles have been reviewed by Sankar *et al.* [21]. Literature survey reveals that no significant work has been carried out so far on the catalytic activities of metal hexacyanidocobaltates. However, we are interested in exploring a series of transition metal hexacyanidoferrates and hexacyanidocobaltates as heterogeneous catalyst for oxidation of aromatic alcohols. Recently, we have reported the catalytic behaviour of nanostructured zinc and nickel hexacyanidoferrates for oxidation of benzyl alcohol under solvent-free and heterogeneous conditions [22, 23]. In the present article, we describe the results of our study on synthesis of nanostructured manganese hexacyanidocobaltate(III) and its catalytic activity for solvent-free oxidation of benzyl alcohol. The catalytic oxidation of benzyl alcohol is an important industrial process as its oxidation product, namely, benzaldehyde is widely used as starting material in synthesis of flavors, cosmetics, perfumes, medicines and so many other chemicals. In recent years, transition metal based heterogeneous catalysts have been reported for these reactions [24-29].

## 2. EXPERIMENTAL

### 2.1. Chemicals and Reagents

K<sub>3</sub>[Co(CN)<sub>6</sub>] was purchased from Across and Mn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, CTAB, C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>OH and H<sub>2</sub>O<sub>2</sub>(30%)

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were purchased from Merck. All chemicals were of analytical reagent grade and used as received. Doubly distilled water was used throughout the experiment.

## 2.2. Synthesis of Nanostructured Manganese Hexacyanidocobaltate(III)

Nanostructured manganese hexacyanidocobaltate(III) was synthesized using a reported method [13]. A 600 ml of 0.001 M  $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  solution containing equimolar quantity of CTAB was slowly added into a 400 ml of 0.001 M  $\text{K}_3[\text{Co}(\text{CN})_6]$  solution at room temperature with a constant stirring. After complete mixing of solutions, the reaction mixture was allowed to stand as such for 1 h. It was then filtered on Buckner funnel, washed thoroughly with distilled water and dried in an oven at 60 °C for 24 h. The solid material so obtained was grinded with pestle mortar and sieved with 100 mesh size.

## 2.3. Instrumentation

An Elementar Vario EL-III CHNS analyzer and a Perkin Elmer atomic absorption spectrophotometer were used to determine the percentage of different elements present in the synthesized material. A Perkin Elmer analyzer system (Pyris Diamond) was used for TGA/DTA studies. Infrared spectra were recorded in KBr disc using Perkin Elmer Spectrophotometer. The particle size was determined using a transmission electron microscope (TEM). A Thermoelectron gas-chromatograph with a HP-1 capillary column (30 mm × 0.25 mm × 0.25 μm) and FID detector was used for the quantitative analysis of  $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$  and  $\text{C}_6\text{H}_5\text{CHO}$ .

## 2.4. Catalytic Activity Studies

Catalytic activity of synthesized material for oxidation of  $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$  was studied by carrying out the oxidation of  $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$  in a magnetically stirred round bottom flask (25 ml) fitted with a mercury thermometer and a reflux condenser. A small aliquot of reaction mixture was taken out after each 30 minute and centrifuged to remove the catalyst. The supernatant, free from catalyst, was subjected to quantitative analysis using gas chromatography. A leaching experiment was carried out to investigate the heterogeneity of catalyst. The catalyst removed from the reaction mixture was washed thoroughly with distilled water, ethyl alcohol and then acetonitrile to detach all the reactant/product molecules adsorbed on its surface. It was dried in an oven at 80 °C for 2h.

Then, it was used again for the oxidation of  $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$  under optimized conditions.

## 3. RESULTS AND DISCUSSION

### 3.1. Synthesis of Nanostructured Metal Hexacyanidocobaltate(III)

The synthesis of manganese hexacyanidocobaltate(III) nanostructures is very simple. The mixing of a dilute solution of  $\text{Mn}^{2+}$  into a dilute solution of  $[\text{Co}(\text{CN})_6]^{3-}$  resulted the growth of manganese hexacyanidocobaltate(III) nanostructures. The CTAB molecules introduced in the reaction mixture probably facilitated the formation of manganese hexacyanidocobaltate(III) nanoparticles with a uniform shape. For long time, it has been a well known fact that the mixing of a dilute solution of divalent transition metal ion into a dilute solution of  $[\text{Fe}(\text{CN})_6]^{3-}$  leads to the formation of insoluble transition metal hexacyanidoferrates [30]. It has been reported that the transition metal hexacyanidoferrates prepared by above process can be represented by a general formula  $\text{M}_3[\text{Fe}(\text{CN})_6]_2 \cdot n\text{H}_2\text{O}$ , where M stands for an exchangeable transition metal and n stands for number of water molecules [31].

The structural composition of synthesized material was determined by CHNS analysis, atomic absorption spectroscopy and thermogravimetric analysis. The percentage of carbon, hydrogen, nitrogen, manganese, cobalt and water in synthesized material is shown in Table 1 and the TGA/DTA curve is shown in Figure 1. The TGA curve exhibited approximately 10% mass loss upto 140 °C in synthesized material. This mass loss was due to the decomposition of water molecules. It has been reported that metal hexacyanidometallates loss water content on the thermal decomposition upto 160 °C [32]. From the Table 1, it is clear that the experimentally observed values of elemental percentage and thermogravimetric data are approximately same to the theoretical values calculated for  $\text{Mn}_3[\text{Co}(\text{CN})_6]_2 \cdot 3\text{H}_2\text{O}$ . Therefore, it is reasonable to propose its molecular formula as  $\text{Mn}_3[\text{Co}(\text{CN})_6]_2 \cdot 3\text{H}_2\text{O}$ . The TEM studies of the synthesized material showed that it consists of roughly spherical particles with their size ranging from 30 to 60 nm. A TEM image of the synthesized material is shown in Figure 2. The nature of bonding has been studied in terms of infrared spectral studies. It showed a strong peak at 2159  $\text{cm}^{-1}$  which is characteristic peak of  $\text{C}\equiv\text{N}$  group present in the synthesized molecule. A broad band at nearly 3200 to 3500  $\text{cm}^{-1}$  was also observed which is due to O-H group of water molecule present in the interstitial sites of its lattice structure.

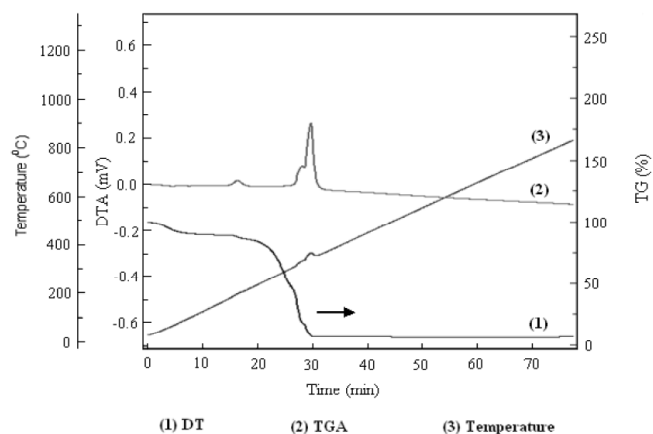
**Table 1: Elemental Analyses of Manganese Hexacyanidocobaltate(III)**

C %	N %	H %	Mn %	Co %	H <sub>2</sub> O %
21.90 <sup>a</sup>	25.18	0.89	25.67	18.54	8.10
(22.41) <sup>b</sup>	(25.56)	(0.77)	(25.31)	(18.31)	(8.30)
{21.96} <sup>c</sup>	{25.40}	{0.82}	{25.52}	{18.45}	{8.18}

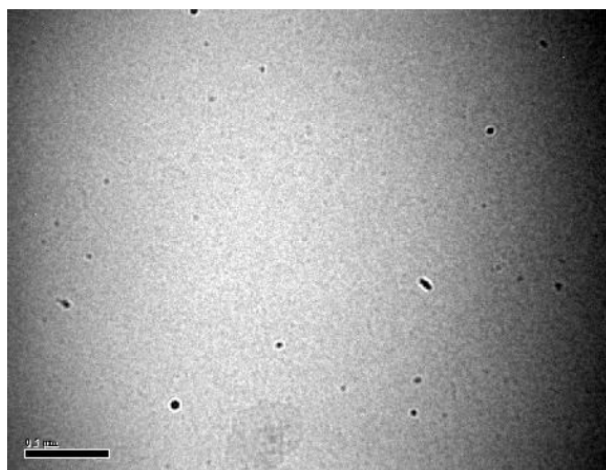
<sup>a</sup> Values without bracket indicates experimentally observed values

<sup>b</sup> Values in small bracket indicates the theoretical values

<sup>c</sup> Values in curly bracket indicates the observed values for recycled catalyst



**Figure 1:** TGA/DTA curve of nanostructured manganese hexacyanidocobaltate(III).



**Figure 2:** TEM image of nanostructured manganese hexacyanidocobaltate(III).

### 3.2. Catalytic Studies

Nanostructured manganese hexacyanidocobaltate(III) was found as an effective heterogeneous catalyst for oxidation of  $C_6H_5CH_2OH$  using  $H_2O_2$  (30%) as oxidant under solvent-free conditions. The catalyst was found to be highly selective towards  $C_6H_5CHO$  as the oxidation product. Blank reaction carried out over the catalyst showed no significant conversion of  $C_6H_5CH_2OH$  into  $C_6H_5CHO$ . Also, no significant

conversion was recorded when the reaction was carried out in absence of catalyst. It proved that neither  $H_2O_2$  can oxidize  $C_6H_5CH_2OH$  in absence of catalyst nor the catalyst can oxidize  $C_6H_5CH_2OH$  in absence of  $H_2O_2$ . The formation of tarry products was not taken into account due to their trivial quantities. Under optimized reaction parameters, the catalyst showed 31% conversion of  $C_6H_5CH_2OH$ .

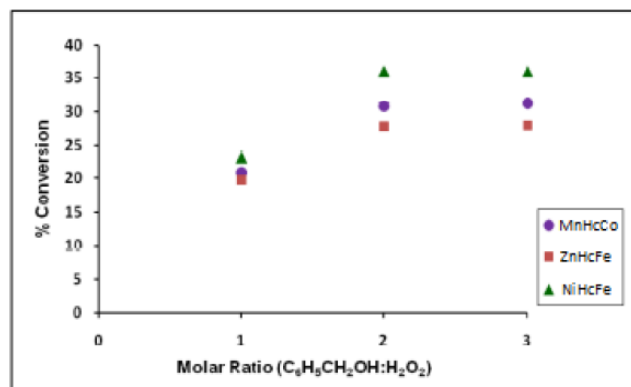
#### 3.2.1. Optimization of Reaction Parameters

The reaction parameters, namely,  $C_6H_5CH_2OH$  to  $H_2O_2$  molar ratio, amount of catalyst, temperature and reaction time were optimized for oxidation of  $C_6H_5CH_2OH$  catalyzed by manganese hexacyanidocobaltate(III). These parameters were optimized by monitoring the percent conversion of benzyl alcohol took place in the reactions on changing one parameter and keeping other parameters constant. The effect of the above parameters has been described as below:

##### 3.2.1.1. Effect of $C_6H_5CH_2OH$ to $H_2O_2$ Molar Ratio

The effect of  $C_6H_5CH_2OH$  to  $H_2O_2$  molar ratio was studied by monitoring the percent conversion of 50 mmol  $C_6H_5CH_2OH$  with different amount of  $H_2O_2$  (30%) (50, 100 and 150 mmol) keeping all other reaction parameters fixed (amount of catalyst = 30 mg, temperature = 75 °C, Time = 3h). It was found that the percent conversion increased significantly on increasing the amount of  $H_2O_2$  (30%) from 50 mmol to 100 mmol. However, the percent conversion was found to be almost constant on further increasing the amount of  $H_2O_2$  (30%) from 100 mmol to 150 mmol. It indicates  $C_6H_5CH_2OH:H_2O_2 = 1:2$  as an optimal molar ratio. This trend of change in percent conversion of  $C_6H_5CH_2OH$  on changing the amount of  $H_2O_2$  (30%) from 50 to 150 mmol was found to be same to that observed in  $Zn_2[Fe(CN)_6] \cdot 3H_2O$  and  $Ni_3[Fe(CN)_6]_2 \cdot 10H_2O$  catalyzed oxidation of  $C_6H_5CH_2OH$  [21, 22]. This trend is likely to be correlated with the amount of oxygen liberated from different amount of  $H_2O_2$  on its decomposition.

Probably, the amount of oxygen liberated using  $C_6H_5CH_2OH:H_2O_2 = 1:1$  was not sufficient to oxidize the total active molecules of  $C_6H_5CH_2OH$ , whereas the amount of oxygen liberated using  $C_6H_5CH_2OH:H_2O_2 = 1:2$  seems to be sufficient to oxidize the total active molecules of  $C_6H_5CH_2OH$ . In case of  $C_6H_5CH_2OH:H_2O_2 = 1:3$ , the amount of liberated oxygen seems to be more than its requirement. The percent conversion data observed using  $Mn_3[Co(CN)_6]_2 \cdot 3H_2O$  and its comparison with previously reported  $Zn_2[Fe(CN)_6] \cdot 3H_2O$  and  $Ni_3[Fe(CN)_6]_2 \cdot 10H_2O$  catalysts has been summarized in Table 2 and Figure 3.

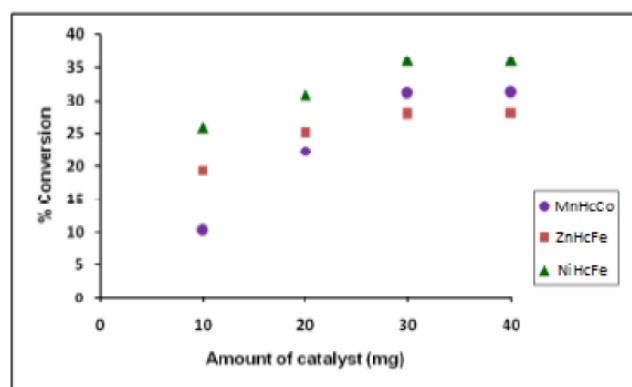


**Figure 3:** Effect of benzyl alcohol to  $H_2O_2$  ratio on percent conversion of  $C_6H_5CH_2OH$ .

### 3.2.1.2. Effect of Amount of Catalyst

The effect of amount of catalyst on percent conversion was studied by changing the amount of catalyst from 10 to 40 mg keeping all other reaction parameters fixed (amount of  $H_2O_2 = 100$  mmol, amount of  $C_6H_5CH_2OH = 50$  mmol, temperature =  $75^\circ C$ , Time = 3 h). The percent conversion was found to be increased on increasing the amount of catalyst from 10 to 30 mg. However, the percent conversion was found to be almost constant on increasing the amount of catalyst from 30 mg to 40 mg. It indicated that 30 mg was the optimal amount of  $Mn_3[Co(CN)_6]_2 \cdot 3H_2O$  catalyst. This drift in percent conversion of  $C_6H_5CH_2OH$  on changing the amount of catalyst is in good

agreement with that of previous observation [21, 22]. This drift can be understood by assuming the percent conversion as a function of the number of catalytic sites available on catalyst surface. It seems that the catalytic sites provided by 10 and 20 mg  $Mn_3[Co(CN)_6]_2 \cdot 3H_2O$  were not sufficient for the adsorption of all the active molecules of reactants, whereas 30 mg  $Mn_3[Co(CN)_6]_2 \cdot 3H_2O$  provided sufficient catalytic sites required for the adsorption of all the active molecules of reactants. However, number of catalytic sites provided by 40 mg  $Mn_3[Co(CN)_6]_2 \cdot 3H_2O$ , probably, exceeds to their requirement. The comparative data of the percent conversion has been presented in Table 2 and Figure 4.



**Figure 4:** Effect of amount of catalyst on percent conversion of  $C_6H_5CH_2OH$ .

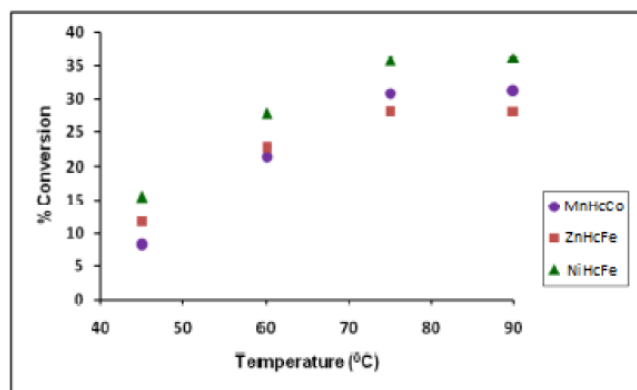
### 3.2.1.3. Effect of Temperature

The effect of temperature on percent conversion was determined by performing the oxidation of 50 mmol  $C_6H_5CH_2OH$  at 45, 60, 75, and  $90^\circ C$  keeping all other reaction parameters fixed (amount of catalyst = 30 mg, amount of  $H_2O_2 = 100$  mmol, time = 3h). The percent conversion was found to be increased on increasing the temperature from 45 to  $75^\circ C$ . However, percent conversion was found to be almost unaffected on increasing the temperature from 75 to  $90^\circ C$ . It indicated that  $75^\circ C$  was the optimal temperature. The same temperature has been found to be optimal for

**Table 2: Effect of  $C_6H_5CH_2OH:H_2O_2$  Molar Ratio and Amount of Catalyst on Percent Conversion**

Catalyst	$C_6H_5CH_2OH:H_2O_2$			Amount of Catalyst (mg)			
	1:1	1:2	1:3	10	20	30	40
$Mn_3[Co(CN)_6]_2 \cdot 3H_2O$	20.9	30.8	31.1	10.2	22.3	31.2	31.3
$Zn_2[Fe(CN)_6] \cdot 3H_2O$	19.7	27.7	27.8	19.4	25.0	27.8	28.0
$Ni_3[Fe(CN)_6]_2 \cdot 10H_2O$	23.0	36.0	36.0	25.8	31.0	36.0	36.0

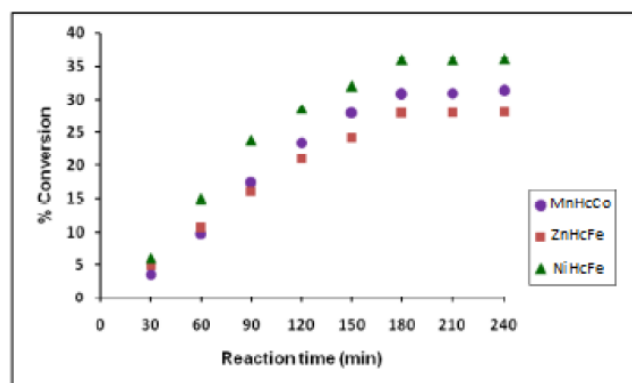
$\text{Zn}_2[\text{Fe}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$  and  $\text{Ni}_3[\text{Fe}(\text{CN})_6]_2 \cdot 10\text{H}_2\text{O}$  catalyzed oxidation of  $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$  [21, 22]. The comparative data has been shown in Table 3 and Figure 5. The change in percent conversion of  $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$  with temperature can be understood on the bases of collision theory as well as the mechanism of heterogeneous catalysis. According to the collision theory, the reaction progress increases on increasing the fraction of active reactant molecules which increases on increasing the temperature. In the mechanism of heterogeneous catalysis, it is assumed that reactant molecules adsorb on the surface of catalyst. Therefore, it is reasonable to suggest that the number of active molecules of  $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$  increased on increasing the temperature from 45 to 75 °C. However, the adsorption probably started to decrease on further increasing the temperature above 75 °C.



**Figure 5:** Effect of temperature on percent conversion of  $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$ .

### 3.2.1.4. Effect of Reaction Time

The effect of reaction time was studied by monitoring the percent conversion at 30, 60, 90, 120, 150, 180, 210, and 240 min keeping all other reaction parameters fixed (amount of catalyst = 30 mg, amount of  $\text{H}_2\text{O}_2$  = 100 mmol, amount of  $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$  = 50 mmol, temperature = 75 °C). The percent conversion was found to increase linearly when the reaction time was increased up to 120 min and was found to increase at a slow rate when the reaction time was increased from 120 to 180 min. Finally percent conversion became nearly constant when the reaction time was increased above 180 min. It indicated that 180 min was the optimal reaction time. The same reaction time has been found to be optimal for  $\text{Zn}_2[\text{Fe}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$  and  $\text{Ni}_3[\text{Fe}(\text{CN})_6]_2 \cdot 10\text{H}_2\text{O}$  catalyzed oxidation of  $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$  [21, 22]. The data of percent conversion at different time has been given in Table 4 and Figure 6.



**Figure 6:** Effect of reaction time on percent conversion of  $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$ .

**Table 3:** Effect of Temperature on Percent Conversion of  $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$

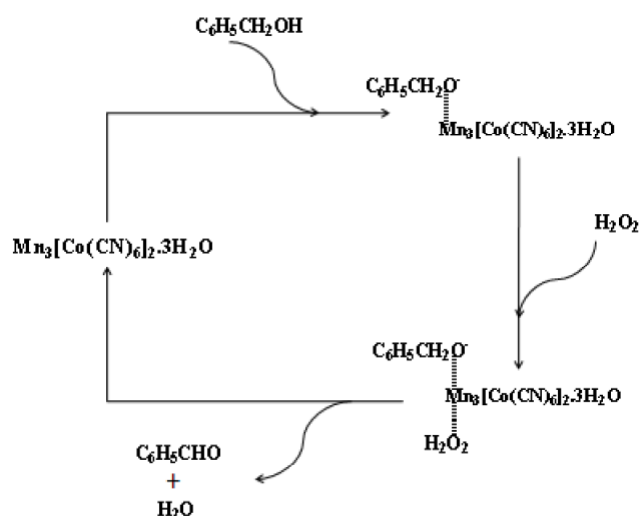
Catalyst	Temperature (°C)			
	45	60	75	90
$\text{Mn}_3[\text{Co}(\text{CN})_6]_2 \cdot 3\text{H}_2\text{O}$	8.2	21.4	30.9	31.2
$\text{Zn}_2[\text{Fe}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$	11.6	22.6	27.9	28.0
$\text{Ni}_3[\text{Fe}(\text{CN})_6]_2 \cdot 10\text{H}_2\text{O}$	15.5	27.7	35.8	36.2

**Table 4:** Effect of Time on Percent Conversion of  $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$

Catalyst	Time (min)							
	30	60	90	120	150	180	210	240
$\text{Mn}_3[\text{Co}(\text{CN})_6]_2 \cdot 3\text{H}_2\text{O}$	3.6	9.8	17.3	23.4	27.8	30.8	31.0	31.3
$\text{Zn}_2[\text{Fe}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$	4.9	10.6	16.1	21.0	24.2	27.8	28.0	28.1
$\text{Ni}_3[\text{Fe}(\text{CN})_6]_2 \cdot 10\text{H}_2\text{O}$	6.0	14.9	23.8	28.6	32.1	36.0	36.0	36.1

### 3.2.2. The Possible Reaction Pathway

Infrared spectral studies were used to propose a probable reaction pathway of  $\text{Mn}_3[\text{Co}(\text{CN})_6]_2 \cdot 3\text{H}_2\text{O}$  catalyzed oxidation of  $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$ . For this purpose, a small aliquot of reaction mixture was taken out after 60 min. The catalyst so collected was subjected to the infrared spectral analysis and its infrared spectrum showed a negligible change in characteristic frequency of  $\text{C}\equiv\text{N}$  group. It confirmed that the reactant molecules did not affect the environment of coordination sphere of catalyst molecule. It means that the reactant species did not interact with  $\text{Co}^{3+}$  present in the coordination sphere. Therefore, it is reasonable to propose that the reactant molecules interacted with outer  $\text{Mn}^{2+}$  and converted into the product. Several aromatic molecules have been found to be adsorbed on metal hexacyanidoferrates due to their interaction with outer metal only [33-35]. Based on this fact, a probable reaction pathway is shown in scheme 1.



**Scheme 1:** Probable reaction pathway of catalytic oxidation of  $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$ .

### 3.2.3. Heterogeneity and Recyclability of Catalyst

A typical leaching experiment was carried out to test the heterogeneity of the catalyst. The filtrate was collected after the removal of catalyst from the catalytic reaction and subjected to atomic absorption spectroscopic studies. The absence of metal in the filtrate of reaction mixture indicated that there was no metal leaching during the catalytic reaction confirming the heterogeneity of catalyst. The recovered catalyst was thoroughly washed, dried and used again for the oxidation of  $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$  under optimized conditions. The recycled catalyst showed 27.8% conversion of  $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$ . Thus, approximately 10% loss was

observed in the percent conversion of using the recycled catalyst.

## CONCLUSION

Manganese hexacyanidocobaltate(III) nanostructures can be grown by slow mixing of a diluted solution of  $\text{Mn}^{2+}$  to a diluted solution of hexacyanidocobaltate(III) ions with constant stirring using CTAB as stabilizer. The synthesized nanostructures acted as heterogeneous catalyst for solvent-free oxidation of benzyl alcohol using  $\text{H}_2\text{O}_2$  as oxidant. It showed 30% conversion of benzyl alcohol into benzaldehyde under optimized reaction conditions used herein.

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