Synthesis and Characterization of a complex mixture based on cobalt and tin and study of its application towards production of hydrogen gas from ethanol

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Abstract. The Cobalt complex, (Co-DMET) has been synthesized from the reaction between cobalt chloride hexahydrate and dimethoxy ethane (DME) in a 1:1 molar ratio and characterized using various measurement techniques. The structural formula of this complex derived based on characterization is [Co(DMET)2(H2O)2]Cl2. 4H2O. Dimethoxy ethane is an O-donating ligand able to coordinate in a chelate mode to the central metal cobalt to form the complex. The bidentate ligand is used to make the complex more stable. This complex was further mixed with the catalytic amount of SnO2 to obtain a complex mixture, (Co-DMET-Sn) and its application towards hydrogen production from ethanol at temperature 333 K was checked. Liberation of H2 gas is found to be maximum at 15 cc of ethanol when charged with 1:0.1 molar ratios of cobalt-DMET complex and SnO2. This same cobalt-DMET-tin mixture was charged with various quantities of ethanol ranging from 5.0 cc to 50.0 cc at temperature 333 K. Amount of H2(g) liberated from ethanol was estimated to be 14.92 % using Gas Liquid Chromatography (GLC). The cobalt is used due to less expensive than the other metals such as Pt which is generally used for catalytic purpose. Crystallite size of the Cobalt-DMET-tin complex was found to be 23.4 nm.

Key words: H2(g), Co-DMET, Co-DMET-Tin, SnO2, GLC, O-donating ligand, Chelate mode.

1. Introduction

Till date, energy extraction from fossil fuel is mostly through conventional techniques, although modern techniques are being employed to minimize production of environmentally harmful by-products. Conventional processes of energy harnessing create a great deal of environmental pollution due to release of greenhouse gases leading to climatic changes [1]. In order to overcome these drawbacks, many researchers are now working in the direction of generating cleaner fuel with extremely less by-products, while extracting energy from the fossil fuels. This prevailing scientific approach encouraged us to try out generating hydrogen fuel whose by-product is only water. We have tried to generate hydrogen gas from ethanol using cobalt-DMET-tin complex. The results thus obtained from the experiments are found to be highly interesting which encouraged us to report those in this manuscript. The H2 gas can be produced from different sources such as fossil fuels, oils, water
and other biomass etc. [1-3]. The production of H$_2$ gas from ethanol in various processes such as partial oxidation, auto-thermal, steam reforming as well as using catalysis is nothing new to this world [4-8]. Byrd et al. found that steam reforming of ethanol not only produce H$_2$ but also some unwanted by-products such as CO and CO$_2$ [4]. This steam reforming is an endothermic process and feasible thermodynamically at high temperatures [9]. Catalysts such as Ni/Al$_2$O$_3$, Ni/La$_2$O$_3$, etc. were used for steam reforming of ethanol at different temperatures, but it also produces the by-product like acetaldehyde along with desired product H$_2$. Fatsikotas et al. also found that the increased in reaction temperature increases the quantity of by-products such as CO, CO$_2$, CH$_4$ along with desired product H$_2$ [10-11]. The dry reforming of ethanol is also highly endothermic and produces some unwanted gas such as CO [12-16]. The SnO$_2$-embedded with K$_2$O or Zeolite Y catalyst was also used for the production of H$_2$ gas from ethanol and the conversion was about 89% but at high temperature of about 873 K [17]. We generated hydrogen from ethanol using 1:0.1 molar ratios of cobalt-DMET complex and SnO$_2$ at very low temperature and dry reforming process. The liberation of hydrogen is about 15%.

2. Experimental

2.1. Materials

Cobalt chloride hexahydrate (Merck, ACS reagent grade, CAS: 7791-13-1, Assay 98%), 1,2-Dimethoxyethane (DMET) (Anhydrous grade, Sigma Aldrich, CAS: 110-71-4, Assay 99.5%), Tin (IV) oxide (Sigma Aldrich, CAS: 18282-10-5 Assay ≥ 99.99%) and ethanol (Merck, ≥ 99.5%, CAS: 64-17-5) were used without further purification.

2.2. Physical measurements

The pH measurement was carried out using Elico LI-617 pH meter equipped with a combination of glass-Ag electrode glass Ag/AgCl (3mol dm$^{-3}$ NaCl solution). The calibration of pH meter was carried out using standard procedure. The quantitative estimation of Cobalt and Tin were carried out with Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES) with iCAP – 6500 DUOICP – OES, thermo scientific system. The mixture was dissolved in 10 cc HNO$_3$ at 30% (v/v) and the volume was made up to 100 cc using high-performance liquid chromatography (HPLC)-grade water for elemental analysis. Electron spray ionization – Mass spectrometry (ESI-MS) was carried out by a Thermo Scientific Exactive-2011 system coupled with an Orbitrap Analyzer. JEOL JSM-7610F microscope was used for capturing Field Emission Scanning Electron Microscopy images of the complex. Gas Liquid Chromatography (GLC) was carried out by Nucon-GC 5700 equipment. The detection of H$_2$ gas was carried out using helium as the carrier gas and TCD-thermal conductivity detector was used. Bruker D8 Advance was used to carry out the Powder X-ray Diffraction (PXRD) which was performed at ST & IC, Cochin University of Science and Technology, Cochin Kerala. The ICP-OES, FE-SEM, ESI-MS and GLC were performed at Indian Institute of Chemical Technology (IICT) - Hyderabad.

The Cobalt-DMET-tin mixture was taken in a 500 ml. round bottom flask. The gas was generated with addition of ethanol to the above cobalt-DMET complex along with catalytic amount of tin (IV) oxide at 333 K, without addition of water. The continuity of the gas evolution from the mixture present in reactor was persisted up to ~ 30 minutes. Initially the gas evolved very violently and then decreased towards the end. The gas volume was measured with respect to time using two inverted burettes containing double distilled water. These burettes were connected with 500 ml. reactor using tube. The evolved gas was collected in a 1-liter Tedlar sample bag with polypropylene fitting (Cat. No. 232.01; Batch: 78029). The hydrogen gas is not dissolved in distilled water at room temperature. So, the first burette was filled with distilled water. As the gases evolve, the water level of first burette decreases while the water level of second burette
increases. The amount of gas evolved was measured using the decrease of water level in the first burette. This volume was cross checked with the increase of water level in the second burette. No error was detected in between the difference of water volume in both the burettes. The method of collection and measurement of gas is represented in outline as Figure 1. The various amounts of ethanol i.e. from 5.0 cc to 50.0 cc was used in different batches keeping the amount of cobalt-DMET-tin complex same in each batch.

![Fig. 1: The outline for collection and measurement of gas](image)

2.3. Synthesis of Cobalt-DMET complex
Cobalt chloride hexahydrate was mixed with 1,2-dimethoxyethane (DMET) in 1:1 molar ratio. The solution turned into light blue colour. It was stirred for 30 min in room temperature in order to make it homogeneous. The temperature of the solution was increased to 363 K with stirring for two hours. The color of the solution changed to dark blue. The stirring was continued for further 48 hours without heating. Then the solution was filtered, followed by evaporation to dryness. The purple colour crystals were obtained. Yield of the precipitation was 96%.

2.4. Synthesis of Cobalt-DMET-tin mixture
The physical mixture was prepared using synthesized Cobalt-DMET complex with tin (IV) Oxide in 1:0.1 molar ratio. It was stirred for 30 minute in room temperature in order to make it homogeneous.

3. Results and Discussion

3.1. Micro-elemental analysis
3.1.1. ICP-OES analysis
The element cobalt in Co-DMET complex is quantified using ICP-OES. The experimental and theoretical values for cobalt well coincides with each other. The composition and molecular weight of complex is \([\text{Co(DMET)}_2(\text{H}_2\text{O})_2]\text{Cl}_2\text{H}_2\text{O}\) and 418.14 g./mol, respectively. The calculated and experimental value of cobalt is 14.09 % and 14.22 %, respectively. Similarly, the element cobalt is quantified after the liberation of \(\text{H}_2\) gas. The composition and molecular weight is
[Co(DMET)$_2$ (H$_2$O)$_2$]Cl$_2$·22 C$_2$H$_5$OH and 1430.14 g./mol, respectively. The calculated and experimental value of cobalt is 4.12 % and 3.93 %, respectively. The amount of ethanol was varied in order to coincide with the experimental value of cobalt.

3.2. FTIR analysis

3.2.1. Cobalt-DMET complex

The vibrational bands of DMET ligand at 982 cm$^{-1}$ and 938 cm$^{-1}$ are completely obscured in the Co-DMET complex. This indicates that the conformation of DMET ligand changes during complex formation [18-19]. Fowles et al. and Snijder et al. confirmed that when DMET is applied as chelating agent then it is converted into gauche (tgt) conformation [20-21]. This tgt conformers are highly stable in the liquid state [22]. The C-O stretching frequency band at 1131 cm$^{-1}$ [23], 1155 cm$^{-1}$ [24] and 1022 cm$^{-1}$ [25] of DMET is shifted to 1125.05 cm$^{-1}$ post complexation. The COC bending vibration of DMET is shifted to 472.13 cm$^{-1}$, which is slightly higher than that reported by Heijer and Driessen [26]. The bending frequency of the dimer water molecule is shifted down to 1624.07 cm$^{-1}$ from 1640 cm$^{-1}$ of monomer water molecule [27]. This indicates that there is a dimer water molecule is present in Co-DMET complex. Occurrence of the dimer is further conformed due to presence of a band at lower frequency at 601.30 cm$^{-1}$ [27]. The stretching and bending mode of hydrogen bond are attributed to 670.64 cm$^{-1}$ [27] instead of 700 cm$^{-1}$. The intra-molecular O-H stretching frequency is observed at 3405.42 cm$^{-1}$. The IR spectrum of cobalt-DMET complex is displayed in Figure 2.

Fig. 2: IR spectrum of Co-DMET complex.

3.2.2. Cobalt-DMET-tin complex

The COC bending vibration of Cobalt-DMET-tin complex is shifted downward to 445.06 cm$^{-1}$ as compared to Cobalt-DMET complex but slightly higher than that reported by Heijer and Driessen [26]. The C-O stretching frequency that appear in Cobalt-DMET complex at 1125.05 cm$^{-1}$ is converted to shoulder in stretching and bending mode of water band. The dimer mode of water
molecule is also present in this tin associated complex at 588.89 cm\(^{-1}\) instead of 601.30 cm\(^{-1}\) of cobalt-DMET complex [27]. The stretching and bending mode of hydrogen bond are attributed at 652.05 cm\(^{-1}\) as compared to 670.64 cm\(^{-1}\) of cobalt-DMET complex [27]. The broad band at 3410.10 cm\(^{-1}\) is attributed to intermolecular stretching vibration of hydroxyl group. This is also further conformed from the strong band at 1634.06 cm\(^{-1}\) instead of 1627 cm\(^{-1}\) reported by Malik et al. [28]. The broad band indicates that ethanol from which H\(_2\) is liberated form intermolecular hydrogen bonding with cobalt-DMET-tin complex at room temperature. The IR spectrum of cobalt-DMET-tin complex is displayed in Figure 3.

![IR spectrum of Co-DMET-tin complex](image)

**Fig. 3:** IR spectrum of Co-DMET-tin complex

### 3.3. X-ray crystallographic analysis

The PXRD pattern of cobalt-DMET-tin complex, \([\text{Co(DMET)}_2(\text{H}_2\text{O})_2]\text{Cl}_2\text{H}_2\text{O}\cdot 22\text{C}_2\text{H}_5\text{OH}\), is displayed in Figure 4.

![PXRD pattern of cobalt-DMET-tin complex](image)

**Fig. 4:** PXRD pattern of cobalt-DMET-tin complex
The diffraction pattern of SnO$_2$ which is used as catalyst is identified using Joint Committee on Powder Diffraction Standards (JCPDS # 41-1445).

3.3.1. Crystallite size determination
The crystallite size of this cobalt-DMET-tin complex was determined using very well known the Debye-Scherrer formula. The crystallite size is 23.4 nm which is very less than the crystallite size of pure SnO$_2$, 60 nm [28]. The micro strain was also calculated using very well known formula of Stokes and Wilson. The formula is given below.

$$\varepsilon_r = \frac{\beta}{4\tan\theta}$$  \hspace{1cm} (1)

The micro strain at $2\theta = 25.179^\circ$ peak is 0.363 which is slightly less as compared to pure SnO$_2$, 0.385 [28].

3.4. FE-SEM analysis
The morphology of cobalt-DMET complex looks like the large flake of cottons that derived from the field emission scanning electron microscopy. In case of cobalt-DMET-tin complex, the morphology looks like the bunch of wet seeds. Both the images are figured in Figure 5. The B part of the figure 5 is more fragile than the figure A. Hence, the surface area of cobalt-DMET complex increases by addition of tin (IV) oxide. As the surface area increases, the catalytic properties of cobalt-DMET-tin complex gets enhanced.

![Fig. 5: SEM Images; figure A indicates cobalt-DMET complex; figure B indicates cobalt-DMET-tincomplex.](image)

3.4.1. ESI-MS fragmentation analysis
The fragmentation pattern of cobalt-DMET complex is figured in Figure 6. Another figure is displayed in Figure 7.
For cobalt-DMET complex the important fragmentation under the experimental condition was the cleavage of DMET to form two methoxy fragments and converted into two mole of methanol m/z 64. These fragments of methoxy group form hydrogen bond with water having m/z 81. This structural fragment is displayed as (I) in Figure 8 and corresponding empirical formula is $C_3H_4O_3$. The next fragment contain 1,2-dimthoxyetane having m/z 90.12 ≈ 91.0. The structural fragment having m/z 111.5 is displayed as (II) in Figure 8 and its empirical formula is $C_3H_8O_2Cl$. This fragment form hydrogen bond with water. The structural fragment containing metal cobalt having m/z 134.9 is displayed as (III) in Figure 8 and its empirical formula is $CoO_2C_3H_4$. The intense fragmentation having m/z 175.9 is displayed as (IV) in above mentioned figure. The empirical formula of this fragment containing cobalt metal is $O_2CoH^-$. The fragment having m/z 225.02 ≈ 225.19 is displayed as (V) in above figure and the corresponding empirical formula containing metallic cobalt is $CoO_4C_3H_8$. Another fragment having m/z 332.8 ≈ 332.14 is displayed as (VI) in above figure and empirical formula containing metallic cobalt is $CoO_6C_3H^-$. The last fragment
having \( m/z \) 431.8 ≈ 431.23 and its structural unit is displayed as (VII) in Figure 8. The empirical formula containing cobalt is \( \text{Co}_2\text{O}_{12}\text{C}_8\text{H}_{28} \).

The fragmentation pattern of cobalt – DMET – tin complex is presented in Figure 9.

![Fig. 9: ESI-MS of Co-DMET-tin complex.](image)

For cobalt-DMET-tin complex the important fragmentation under the experimental condition was also the cleavage of DMET to form two methoxy fragments and converted into two mole of methanol \( m/z \) 64. The fragmentation having \( m/z \) 91.0 is displayed as (I) in Figure 10.

![Fig. 10: The structural fragmentation of Co-DMET-tin complex.](image)
In this fragmentation pattern, the ethoxide ion forms hydrogen bond with ethanol which is used in the reaction as solvent. The empirical formula for this fragmentation is $\text{C}_2\text{H}_5\text{O}_2$. The fragmentation having $m/z$ 150.71 $\approx$ 150.10 belongs to $\text{SnO}_2$. The intense fragmentation having $m/z$ 225.02 $\approx$ 225.19 is same as that of cobalt-DMET complex. This structural fragmentation is displayed as (V) in Figure 8. The next fragment having $m/z$ 284.02 $\approx$ 284.26 and its structural unit is displayed as (II) in Figure 10. The empirical formula of the fragment containing cobalt is $\text{CoO}_5\text{C}_{10}\text{H}_4$. This fragment when hydrated with three aqueous molecules gets converted into fragment having $m/z$ 338.02 $\approx$ 338.34. The structural unit is displayed as (III) in the figure. The empirical formula is $\text{CoO}_8\text{C}_{13}\text{H}_4$. The above given fragment when hydrated with two aqueous molecules as well as ethoxy forming hydrogen bond with coordinated water molecule, while the methoxy form covalent bond with the free radicals of the structural unit (III). The structural unit of the above fragment is displayed as (IV) in Figure 10. The empirical formula containing cobalt is $\text{CoO}_{12}\text{C}_{13}\text{H}_{35}$ and having $m/z$ 450.02 $\approx$ 449.38.

3.5. Gas Liquid Chromatography (GLC)

The retention time versus voltage graph was plotted for the detection of $\text{H}_2$ in Gas Liquid Chromatography (GLC). The collected gas contains 14.92 % hydrogen. Quantification of $\text{H}_2$ liberated with various quantity of ethanol was carried out in water. The $\text{H}_2$ is not absorbed in water. The chromatogram is displayed in Figure 11.

![Chromatogram](image)

**Fig 11: GLC Chromatogram**

3.5.1. Estimation of hydrogen liberation

0.01 mol. of cobalt –DMET complex is mixed with 0.001 mol. of $\text{SnO}_2$ for the production of $\text{H}_2$ from ethanol. In this experiment, the same proportion of cobalt-DMET complex and $\text{SnO}_2$ is mixed with various proportion of ethanol from 5.0 cc to 50.0 cc. It has been found that the maximum quantity
of H₂ liberated is 68.8 cc at 15.0 cc of ethanol. The quantity of H₂ liberation increases with increase of addition of ethanol from 5.0 cc to 15.0 cc then decreases with increase of addition of ethanol. The quantity of H₂ liberated is 9.0 cc, 35.5 cc, 68.8 cc, 30.5 cc, 34.0 cc, 47.2 cc, 18.8 cc and 15.1 cc with respect to volume of ethanol 5.0, 10.0, 15.0, 20.0, 25.0, 30.0, 35.0, 40.0 and 50.0 cc, respectively. The abnormality of H₂ liberation after 15.0 cc of ethanol may be due to the formation of hydrogen bonding of ethoxy with the cobalt-DMET complex. The liberation of H₂ depends upon the degree of hydrogen bonding of ethoxy group. The formation of ethoxy hydrogen bonding with cobalt-DMET-tin complex is confirmed not only from the ESI-MS fragmentation pattern, Fig 10, but also from the FTIR analysis of cobalt-DMET-tin complex, which shows broad band at 3410 cm⁻¹.

4. Conclusion

The cobalt-DMET complex was synthesized and characterized with different measurement techniques such as FT-IR, ICP-OES, PXRD and ESI-MS. The quantity of liberation of H₂ from ethanol is measured using GLC. The 1:0.1 ratios of cobalt-DMET and tin (IV) oxide were used repeatedly for the liberation of hydrogen using various quantity of ethanol ranging from 5.0 cc to 50.0 cc at temperature 333 K. The maximum liberation of H₂ takes place when 15 cc of ethanol is charged with 1:0.1 molar ratios of cobalt-DMET complex and SnO₂ at 333 K.

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