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Synthesis and Characterization of Hybrid Salt of Silicomolybdate Cluster: Heterogeneous Catalysis and UV-Kinetics

G. Priyanka, C. Sabarinathan, S. Pitchaimuthu, T. Arumuganathan*

Department of Chemistry, Thiagarajar College, Madurai – 625 009, Tamilnadu, India.

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ABSTRACT

Novel inorganic-organic hybrid cluster is constructed by polyoxometalate (POMs) and iron coordination complex. Iron coordinated complex (ML_1) has been synthesized by reacting iron(II)sulphate with N,N dimethylethylenediamine and salicylaldehyde in methanol. Synthesized complex $[M(L_1)_2]$ (1) where M = Fe^{2+}coupled subsequently with $H_4SiMo_{12}O_{40}$ in presence of nitric acid. Oxidation of Fe^{2+} into Fe^{3+} leads to the formation of a cationic species $[Fe(L_1)_2]^+$ which is stabilized *in situ* by the presence of bulky $[SiMo_{12}O_{40}]^{4-}$ anion. Precipitated inorganic-organic hybrid $[Fe(L_1)_2]_4[SiMo_{12}O_{40}]$ (2) has been characterized by UV-Visible spectroscopy, IR spectroscopy, PXRD, Cyclic Voltammetry (CV), and thermogravimetric analysis (TGA). The hybrid material is also investigated towards the oxidation of secondary alcohol to corresponding ketone in the presence of hydrogen peroxide. The product formation has been monitored by TLC and UV-visible spectroscopy. Investigation on kinetic aspects was performed for the aforementioned organic conversion by using UV-Visible spectrophotometer. The catalysis used in this study is in heterogeneous fashion and concluded that catalyst can be reused minimum three times without altering the product conversion.

1. Introduction

Polyoxometalate (POM) is a metal-oxo cluster mostly formed by inner-transition elements such as molybdenum, tungsten and vanadium with oxygen [1]. From the back history of POM it is well known that research activities triggered in multiple directions such as catalysis [2] medicine [3] conductance [4] supramolecular chemistry [5] charge transfer salts [6] etc. since the day of POM cluster structurally characterized by Keggin [7]. Fascinating structures and gorgeous architectures of POMs family is continuously attracting research community to larger extent [8]. Especially investigating the catalytic application of POM cluster is more interested because of the following advantages that documented in the literature such as POM clusters are (i) oxidatively resistant (ii) can withstand higher temperature (iii) more selectivity (iv) economically cheaper (v) can be used as heterogeneous catalyst and hence reusable (vi) contains large numbers of potential coordination sites (both terminal and bridging oxygen atoms and hence surfaces are the main source for their multifunctional catalytic activity. In the present work we designed, synthesized and characterized inorganic-organic hybrid material in which iron coordinated complex acts as cation and silicomolybdic acid as anion. Hybrid material can be formulated as $[Fe(L_1)_2]_4[SiMo_{12}O_{40}]$ (2) where Fe = in Fe^{3+} state and L_1 = Schiff base formed from N,N dimethylethylenediamine and salicylaldehyde. Compound 2 is investigated for their catalytic activity towards the oxidation of secondary alcohol to ketone/carbonyl conversion in heterogeneous phase and hence reusable.

Recycling of catalyst is considered most important in cost and economic point of view. In the direction of reprocessing, heterogeneous catalyst is to be considered more advantages than from the homogeneous phase. In this aspect regenerating a catalyst from its homogeneous phase is complicated. It needs special technique such as filtering catalyst through immobilized solid support [9] and nano filtration by enlarging the molecular structure of catalyst [10] etc. thereby in reality the performance of catalyst may also be affected. Hence such kind of hurdles may be resolved by designing suitable heterogeneous catalysts. Accordingly, there is a requirement of readily accessible heterogeneous catalyst that should be able to use in multiple times. It is common that POM catalyst needed a suitable oxidant for their successful oxidation. Even though many number of oxidants available in the literature such as molecular oxygen, $NaIO_4$, tBuOOH etc., there are some demerits that should be considered seriously such as fire capture/explosion behavior, selectivity, wastages amount and cost etc. By taking into account of all those things we considered hydrogen peroxide as green catalyst because it is cheaper and above all it produces water and molecular oxygen on decomposition. Usage of POM as catalyst is found to be massive in literature that includes hydrogen peroxide as oxidant [11] Advantages of using hydrogen peroxide as oxidant is evidenced in the literature [12]. We are interested for the conversion of 1-phenyl ethanol to its corresponding carbonyl compound acetophenone because later one industrially most wanted ketone such as perfume, aromo industries etc. [13].

2. Experimental Methods

2.1 Materials and Instrumentation

All the chemicals used in research work were obtained from S.D. Fine, Merck and Loba etc. used without any further purification. $H_4SiMo_{12}O_{40}$ was prepared by following available literature procedure [14]. Distilled water was used throughout the experiment. 1-phenylethanol is prepared by the reduction of commercially available acetophenone with $NaBH_4$ in methanol. UV spectrum of the complex $[Fe(L_1)_2]$ and cluster ($[Fe(L_1)_2]_4[SiMo_{12}O_{40}]$) was studied in the range of 200 – 800 nm with the help of JASCO UV-530 spectrophotometer. FT- IR spectrum recorded in JASCO FT-IR 6300 spectrometer. Cyclic voltammogram was recorded in 680 Amp Booster model. Compound 2 was dissolved in mixture of dimethyl formamide and water with approximate ratio of 1:10 in respectively that containing 0.1 M solution of potassium chloride (KCl) as the supporting electrolyte. We used glassy carbon electrode as a working electrode with surface area of 0.035 cm^2, platinum wire as the counter electrode and Ag wire used as reference electrode. Thermo Gravimetric Analysis (TGA) data obtained from SHIMADZU -TA 60 model instrument. The measurement carried out under N_2 flow between the temperature ranges of 30 – 800 °C at the heating rate of 10 °C / minute. Kinetics study of catalytic conversion of 1-phenylethanol to acetophenone completed with JASCO UV-530 spectrophotometer.

*Corresponding Author
Email Address: arumuganathan_chem@tcarts.in (T. Arumuganathan)

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2.2 Synthesis

2.2.1 Synthesis of [Fe(L₁)₂] (1)

The outline of synthesis of complex ([Fe(L₁)₂]) and cluster ([Fe(L₁)₂]₄[SiMo₁₂O₄₀]) is depicted in Fig. 1. Synthesis procedure of [Fe(L1)2] is described as follows: In a 25 mL round bottom flask, salicylaldehyde (2 mmol; 0.214 mL) was added to a solution of N,N-dimethylethylenediamine (2 mmol; 0.216 mL) and left stirring for 15 minutes in acetonitrile (10 mL). Then iron(II)sulphate heptahydrate (1 mmol; 0.278 g) was added to the previous mixture and left stirring for 1 hour. Obtained precipitate was filtered, washed well with water and dried in vacuum and then stored in vacuum desiccator; yield: 1.840 g.

2.2.2 Synthesis of [Fe(L₁)₂]₄[SiMo₁₂O₄₀] (2)

The precipitate formed in afore mentioned procedure [Fe(L₁)₂] (1) is taken as starting precursor for the synthesis of compound 2. Compound 1 (0.4 mmol; 0.175 g) is dissolved in 10 mL methanol and to this mixture about 1 mL of nitric acid was added. The resulting solution was stirred for one hour. To the resulting mixture silicomolybdic acid [$H_4SiMo_{12}O_{40}$; 0.1 mmol; 0.184 g] was added further stirring continued for one hour. During the course of the reaction time formed yellow precipitate was filtered, dried in vacuum and then stored vacuum decicator; yield: 0.520 g.

2.2.3 Synthesis of 1-Phenylethanol from Acetophenone

To the ice cold solution of acetophenone (15 mL, 0.13 mmol) in 30 mL of methanol about $NaBH_4$ (10 g, 264 mmol) was added stepwise slowly. The reaction mixture was allowed to stir till the effervescence stopped. Then the reaction mixture was refluxed for two hours. Mixture then extracted with dichloromethane solvent. The collected extract was dried with magnesium sulphate and then filtered. After evaporation of solvent 1-phenylethanol obtained was stored in a closed vial. The product 1-phenylethanol is confirmed by TLC and UV.

3. Results and Discussion

3.1 Structure Discussion

3.1.1 [Fe(L₁)₂] (1)

Neutral complex 1 is synthesized by reacting $FeSO_4$ with Schiff base (L_1). Ligand (L_1) is designed by the condensation reaction of N,N dimethylethylenediamine and salicylaldehyde. Many attempts to derive single crystal fail to produce quality crystal. The anticipated molecular structure of complex 1 is proposed in Fig. 1. The structure of complex 1 is proposed based on the similar compound available in the literature [15]. Structure of 1 reveal that it consists a mononuclear discrete neutral unit [Fe(L_1)$_2$]. The Iron(II) center in a six coordination octahedral environment being coordinated through three arms of Schiff base constructed by ONN fashion suggestive of pincer coordination. Salicylaldehyde condensed with N,N-dimethylethylenediamine produce one imine bond. Oxygen from salicylaldehyde moiety, imine nitrogen (sp^2) and nitrogen (sp^3) atom of N,N-dimethylethylenediamine generate ONN bonding environment. It neutralizes positive charge on Iron(II) center partially by one bridging oxygen and hence further it needs an additional assembly of L_1 ligand for to complete charge and coordination number fulfillment.

3.1.2 [Fe(L₁)₂]₄[SiMo₁₂O₄₀] (2)

Inorganic-organic hybrid compound 2 can be isolated as brown colored solid by reacting compound 1 with silicomolybdic acid in presence of nitric acid. The same reaction carried out in absence of nitric acid does not produce compound 2. This result reveals that Fe(II) center in complex 1 instantaneously oxidized to Fe(III) by the addition of nitric acid and hence generating a cationic version of complex 1 as $[Fe(L_1)_2]^+$. In order to stabilize charge compensation of complex 1, bulky anion $[SiMo_{12}O_{40}]^{4-}$ produced by the ionization of $H_4SiMo_{12}O_{40}$ cluster. Four negative charge of cluster unit reimbursed by four discrete unit of complex 1 because each complex carries a unit positive charge. Subsequently isolated inorganic-organic hybrid material can be formulated as [Fe(L_1)$_2$]$_4$[$SiMo_{12}O_{40}$] (2). Overall synthesis procedure of compound 1and 2 is given in the Fig. 1.

Formed cationic complex $[Fe(L_1)_2]^+$ could not be able to isolated in absence of bulky anion and hence it coupled *in situ* with silicomolybdic acid. Further the same is evidenced from failure of various attempts to isolate complex 1 directly starting from $FeCl_3$ where iron atom is in +3 oxidation state. We believe that it occurred because of necessary of bulky anion to stabilize the cationic species. Representative conventional picture of silicomolybdate anion is given in Fig. 2.

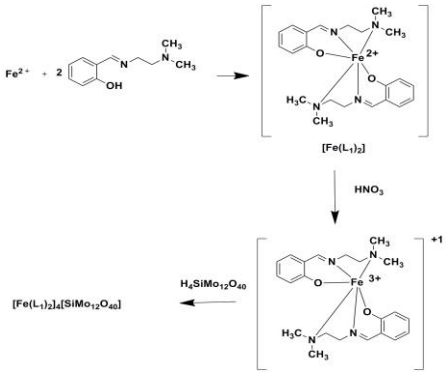

Fig. 1 Schematic diagram of synthesis of [Fe(L_1)$_2$]$_4$[$SiMo_{12}O_{40}$] (2)

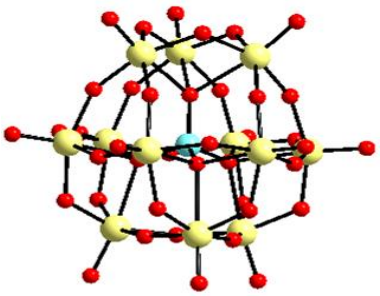

Fig. 2 Ball-Stick model of [$SiMo_{12}O_{40}$[$^{4-}$; Color Code: O, red; Mo, yellow; and Si, cyan.

We have not performed a chemical reaction of $FeCl_3$, $H_4SiMo_{12}O_{40}$ and ligand (L_1) all together in a single reaction. Because, reaction of transition metal ions example Fe^{3+} with POM cluster may leads to substitution of metal in lacunary POM. It produces complicated non-stoichiometric compounds that cannot be resolved easily without collecting single crystal data.

3.2 UV-Visible Spectroscopy

UV-Visible spectrum of complex 1 and inorganic-organic hybrid compound 2 recorded in mixture of solvent with 1:20 in dimethylformamide (DMF) and water respectively from 250 to 800 nm. Complex 1 shows two absorption maxima at 312 nm and 672 nm (Fig. 3). These absorptions are assigned due to imine to metal charge transition and d-d transition respectively. The same observation is found in hybrid compound 2 (Fig. 4). It confirms that the presence of complex 1 moiety in compound 2.

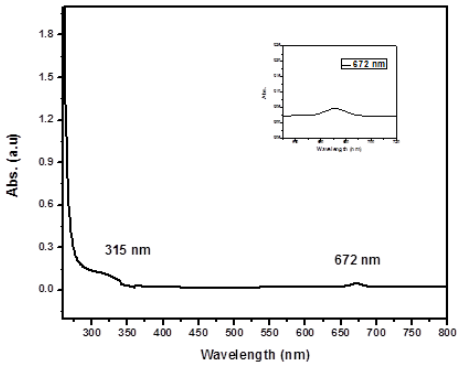

Fig. 3 UV-Visible spectrum of [Fe(L_1)$_2$] (1)

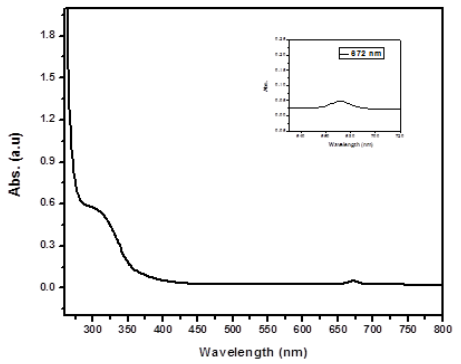

Fig. 4 UV -Visible spectrum of [Fe(L_1)$_2$]$_4$[$SiMo_{12}O_{40}$] (2)

3.3 FT-IR Spectroscopy

FT-IR spectrum of title compound is given in Fig. 5. Characteristic stretching frequencies appeared in 894 and 830 cm^{-1} is due to the presence of molybdenum terminal oxo group (Mo=O). Peak at 1321 is assigned for C-H stretching vibration that originated from ligand. The vibrational bands aroused in the region of 1000 – 1650 cm^{-1} can be assigned to the bending vibrations (either C–H or N–H) or aromatic ring stretching frequencies of the organic ligand. Iron coordinated (C=N) imine stretching frequency that appeared at 1626 cm^{-1}. Phenolic υ_{str}(C–O) stretching allocated at 1312 cm^{-1}.

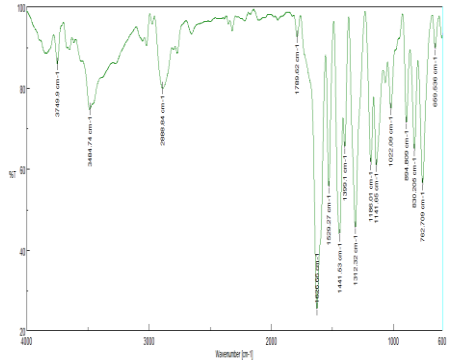

Fig. 5 FT-IR spectrum of $[Fe(L_1)_2]_4[SiMo_{12}O_{40}]$ (2)

3.4 Powder X-Ray Diffraction (PXRD)

Powder X-ray diffraction spectrum of inorganic – organic hybrid compound 2 is presented in Fig. 6. The result shows that the appearance of many diffraction peaks which indicate the complex 2 is polycrystalline in nature. The average crystallite size (D) is calculated from the PXRD data by following Debye-Scherrer equation,

$$D = K\lambda / \beta \cos\theta$$

where λ is wavelength of X-ray radiation (1.541874 Å), K is constant as 0.95 for organic compound and $\beta_{1/2}$ is the half width maximum of the reference diffraction peak that measured in radian. From the average crystallite size (D), dislocation density (δ) can be calculated by using the formula $\delta=1/D^2$. Dislocation density (δ) is defined as the number of dislocation lines per unit area of the crystal. The calculated values of D and δ are documented in the Table 1. The obtained results are closely related with the result reported by Sonbati et al [16].

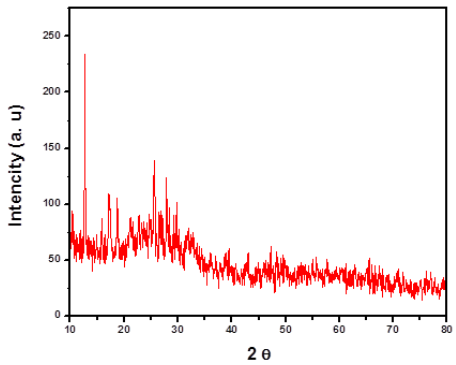

Fig. 6 PXRD pattern of $[Fe(L_1)_2]_4[SiMo_{12}O_{40}]$ (2)

Table 1 PXRD data and analysis of compound 2

S .No	Complex	Average Crystallite Size (D)	Dislocation Density(δ) δ = [1/D²]	Purity	Phase
1	$[Fe(L_1)_2]_4[SiMo_{12}O_{40}]$ (2)	10.12914	9.75 X 10^{-3}	Bulk purity	homogeneous

3.5 Cyclic Voltammetry

Cyclic voltamogram of compound 2 is shown in Fig. 7. In the range of -1.5 to +1.5 (vs Ag / Ag+) compound 2 shows one reversible reduction wave at –1.245 V and one oxidation potential at –1.061 V at the scanning rate of 50 mV/s. The electrochemical behavior of same compound also investigated at various scan rates. Oxidation potential and reduction potential shifted towards positive and negative side respectively upon increasing the scan rate. Their detailed redox potentials and peak currents are given in Table 2. Another oxidation potential wave appeared at -0.501 V is characterized as irreversible. This result is similar to the compound reported by Neumann et al., [17].

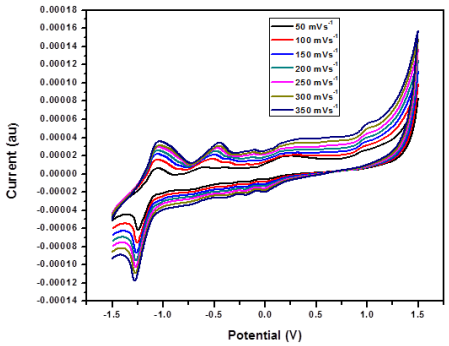

Fig. 7 Cyclic Voltamogram of $[Fe(L_1)_2]_4[SiMo_{12}O_{40}]$ (2)

Table 2 Redox potential and peak current of compound $[Fe(L_1)_2]_4[SiMo_{12}O_{40}]$ (2)

S. No.	Scanning rate mV/sec	Oxidation potential		Reduction potential	
		I/μA	E/V	I/μA	E/V
1.	50	6.041 X 10^{-6}	-1.061	-6.131 X 10^{-5}	-1.245
2.	100	6.041 X 10^{-6}	-1.061	-7.559 X 10^{-5}	-1.254
3.	150	2.19 X 10^{-5}	-1.060	-8.655 X 10^{-5}	-1.261
4.	200	2.593 X 10^{-5}	-1.050	-9.516 X 10^{-5}	-1.265
5.	250	2.938 X 10^{-5}	-1.049	-1.021 X 10^{-4}	-1.269
6	300	3.141 X 10^{-5}	-1.039	-1.095 X 10^{-4}	-1.272
7.	350	3.581 X 10^{-5}	-1.039	-1.117 X 10^{-4}	-1.276

3.6 Thermo Gravimetric Analysis (TGA)

Thermogravimetric analysis was done for compound 1 and 2 in the temperature range of 30 – 800 °C under N_2 flow at 10 °C per minute heating rate. Thermogravimetric analysis (TGA) curve for the complex $[Fe(L_1)_2]$ (1) is depicted in Fig. 8. Typical TG curve shows two weight losses. The first weight loss of 14.60% in the temperature range of 26 - 267 °C is due to the removal of lattice solvent molecules. Second weight loss is not sharp that occurred in the temperature between 274 – 800 °C with 52.63% is due to decomposition of structure and leaves only metal oxide residue.

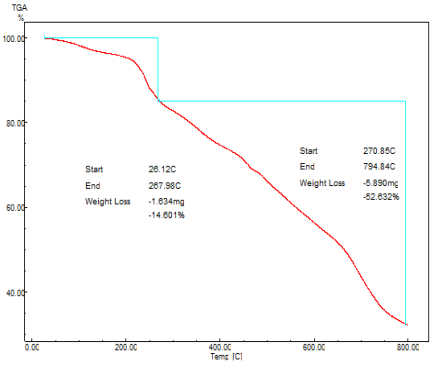

Fig. 8 TGA graph of Complex $[Fe(L_1)_2]$ (1)

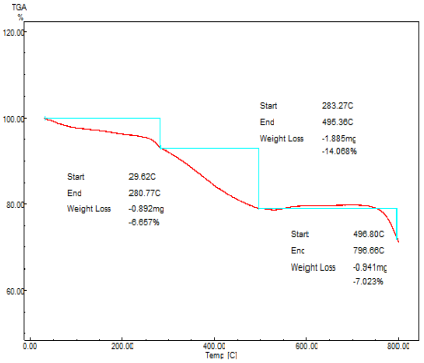

Fig. 9 TGA graph of compound $[Fe(L_1)_2]_4[SiMo_{12}O_{40}]$ (2)

Thermogravimetric analysis (TGA) curve for the inorganic – organic hybrid compound $[Fe(L_1)_2]_4[SiMo_{12}O_{40}]$ (2) is depicted in Fig. 9. Typical TG curve shows three sharp weight losses. The first weight loss of 6.65% in

the temperature range of 30-281 °C is due to the removal of lattice solvent molecules. Second weight loss 14.06% in between 283-495 °C can be assigned due to the loss of organic moiety. The third loss of 7.02% in the range of 497-797 °C is due to the decomposition of structure and leaves only metal oxide residue. The notable difference in the increasing decomposition temperature of title compound 2 is because of the contribution from $[SiMo_{12}O_{40}]^{4-}$. POM cluster stabilizes iron coordinated transition metal complex in their higher oxidation state (refer Fig. 1 for detailed scheme).

3.7 UV-Kinetics of Catalysis

Absorption maximum of 1-phenylethanol is originated at 254 nm, while the same in acetophenone observed in 238 nm (π→π*) and 310 (n→π*). UV-Visible absorption spectra of 1-phenylethanol and acetophenone are depicted in Fig. 10 and Fig. 11 respectively. Based on these differences in UV absorption kinetic study of the transformation of 1-phenylethanol into acetophenone is performed by using title compound 2 in presence of hydrogen peroxide as oxidant.

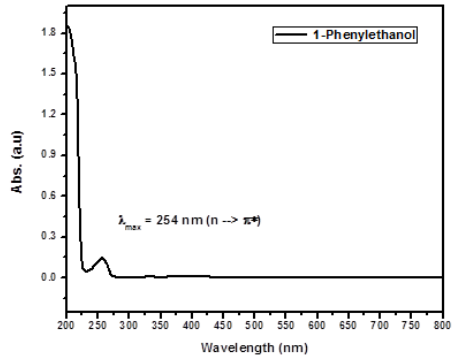

Fig. 10 UV-Visible absorption spectrum of pure 1-phenylethanol

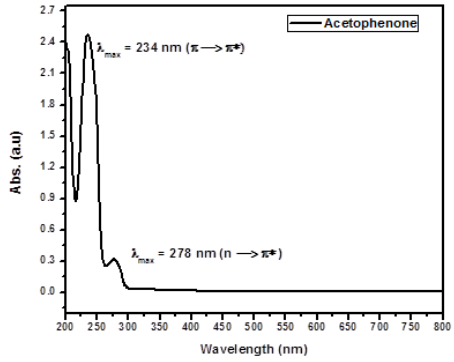

Fig. 11 UV-Visible absorption spectrum of pure acetophenone

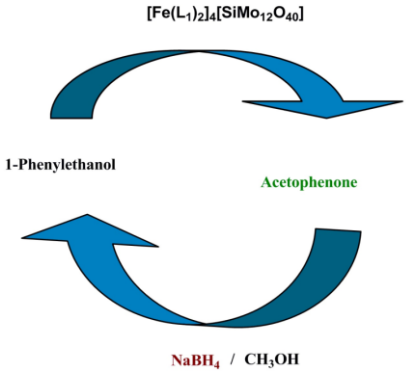

Fig. 12 Schematic representation of conversion of 1-phenylethanol to acetophenone and vice versa

In a representative experiment, the mixture of 1-phenylethanol (0.06 mL, 0.5 mmol), compound 2 (0.08 g, 0.022 mmol), 30% (w/v) of hydrogen peroxide (0.5 mL) and 3 mL of acetonitrile were taken in screwed vial and heated approximately 50 °C for 2.5 hrs. The same reaction was prepared without either catalyst or hydrogen peroxide individually that did not show any remarkable conversion. It undoubtedly indicates the need of both catalyst and hydrogen peroxide for the successful oxidation. Initially, the product formation was monitored and confirmed by TLC. Soon after, the same mixture was transferred to UV spectrophotometer to bring out absorption measurement. The result shows that, the conversion of 1-phenylethanol to acetophenone occurs in moderate yield. Conversion 1-phenylethanol into acetophenone by catalyst compound 2 in presence of H_2O_2 is shown in Fig. 12. At this stage it has been decided to perform a systematic kinetic investigation for this conversion and thereby the results obtained are summarized below.

3.7.1 Investigation on Various Concentration of H_2O_2

Being an oxidant, the concentration of hydrogen peroxide directly has an effect on the conversion of 1-phenylethanol to acetophenone. Conversion amount of alcohol to ketone increases with increasing hydrogen peroxide. During the experiment concentration of catalyst (0.08 g, 0.022 mmol), secondary alcohol (0.06 mL), 3 mL of acetonitrile were kept constant and only hydrogen peroxide varied from 0.3 mL to 1.0 mL in five separate vials [0.3, 0.5, 0.7, 0.9 and 1.0 mL]. Since the inorganic – organic hybrid compound 2 insoluble in acetonitrile catalyst of this work may be described as heterogeneous catalyst. Absorption maximum (λ_{max} at 310 nm) increases on increasing concentration of hydrogen peroxide. Consequent UV-visible absorption spectra are presented in Figs. 13 and 14 respectively. The same absorption peak for pure commercial acetophenone observed at 278 nm. Slight shift is because of impurity effect in reaction mixture. Concentration of hydrogen peroxide with more than of 1.0 mL does not show any notable conversion at these provisions. Requirement of acetonitrile solvent throughout this work is not compulsory for this particular reaction but it is easier and necessary to filter the reaction mixture for carrying out UV absorption studies. Filtered catalyst dried and reused for another set of reaction. Same catalyst can be used minimum three times without affecting the product conversion.

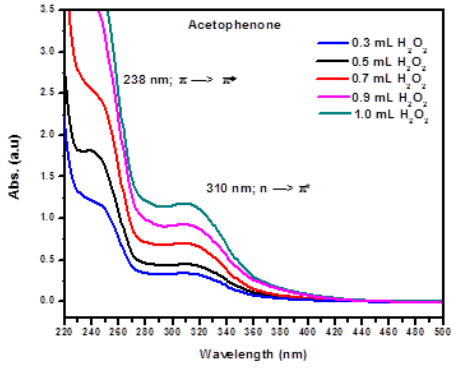

Fig. 13 UV-Visible absorption spectra of conversion of 1-phenylethanol to acetophenone at various concentration of hydrogen peroxide

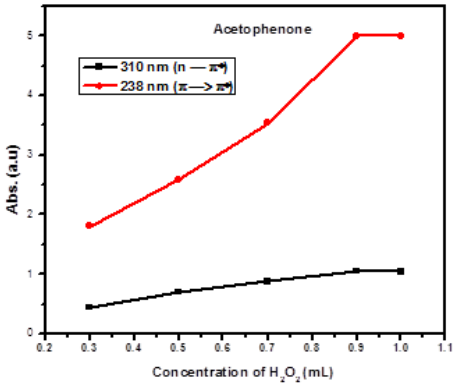

Fig. 14 Plot of various concentration of hydrogen peroxide vs. absorption

3.7.2 Time Variation Catalysis

An experiment was performed by maintaining concentration of catalyst (0.08 g), secondary alcohol (0.06 mL), hydrogen peroxide (0.5 mL) in 3 mL acetonitrile but varying time for the period of 30 minutes to 150 minutes. UV spectrum was recorded for every half an hour and the results were given in Figs. 15 and 16 respectively. Amount of conversion of alcohol to ketone increases with time and reaches saturation at 150 minutes.

3.7.3 Amount of Catalyst Variation

Same experiment was repeated by preserving secondary alcohol (0.06 mL), hydrogen peroxide 0.5 mL) in 3 mL acetonitrile for the period of 150

minutes by varying the concentration of catalyst from 0.04 g (13.33 g /L) to 0.20 g (66.66 g /L) in 3 mL of acetonitrile (13 moles/litre of acetonitrile). The results are given in Figs. 17 and 18 respectively. The result show that alcohol to ketone conversion increases with increasing the catalyst amount gradually and decreases when it reach overloading at 66.66 g /L. This is because when amount of catalyst increases, the substrate contact surface area per unit volume decreases and minimum amount of catalyst surface exposed for the conversion.

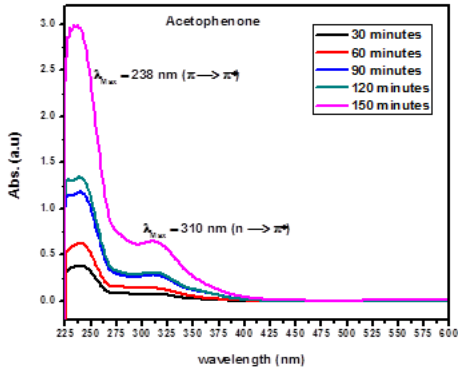

Fig. 15 UV-Visible absorption spectra of conversion of 1-phenylethanol to acetophenone at various time interval

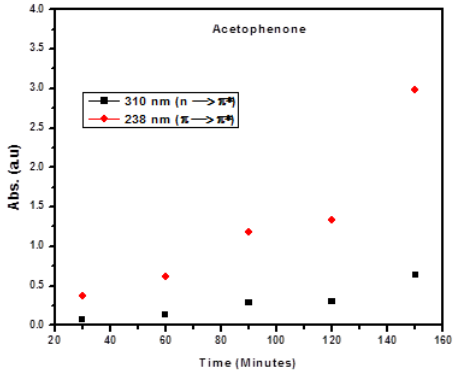

Fig. 16 Plot of various time interval vs. absorption

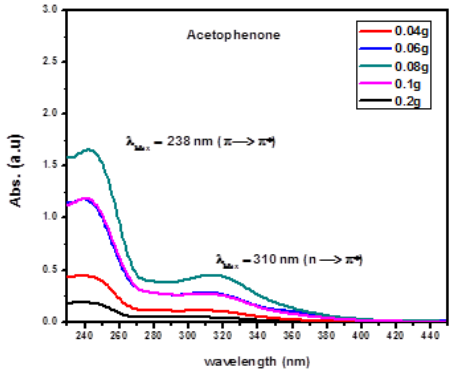

Fig. 17 UV-Visible absorption spectra of conversion of 1-phenylethanol to acetophenone at various concentration of catalyst $[Fe(L_1)_2]_4[SiMo_{12}O_{40}]$ **(2)**

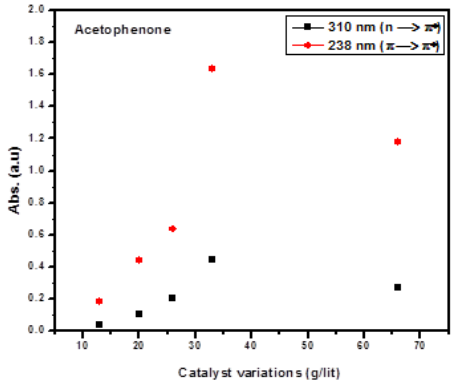

Fig. 18 Plot of various concentration of catalyst $[Fe(L_1)_2]_4[SiMo_{12}O_{40}]$ **(2)** vs. absorption

3.7.4 UV Kinetics

Rate equation of pseudo first order of reaction can be written as

$$\ln[(A_o/A_t) = Kt$$

where A_o = Absorption value of acetophenone (OD) in its initial concentration (0.06 mL in 3 mL of acetonitrile)

A_t = Absorption value of acetophenone (OD) value at particular time
K = Rate constant
t = time taken between two successive UV measurement in minutes

By knowing A_o value, rate constant K is calculated at particular time interval. Obtained results were confirmed that the conversion of 1-phenylethanol to acetophenone in presence of hydrogen peroxide follows pseudo first order kinetics. The slope value is -0.016, intercept value is 1.397 and linear fitting coefficient value is 0.9916. Graph is given in Fig. 19.

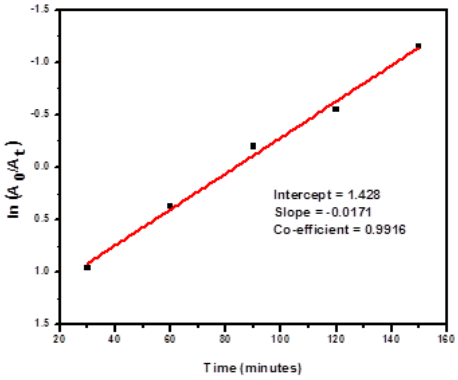

Fig. 19 Plot of [(ln (A_o / A_t)] vs. time

4. Conclusion

We have successfully synthesized and isolated solid material Inorganic-organic hybrid cluster $[Fe(L_1)]_4[SiMo_{12}O_{40}]$ (2) has been isolated and characterized completely by available analytical techniques such as UV-Visible, IR, PXRD, CV and TGA studies. Furthermore, isolated solid cluster has been utilized as catalyst for the conversion of secondary alcohol to their corresponding ketone. Product conversion details investigated through UV kinetics and concluded that organic transformation reaction follows pseudo first order kinetics. By applying same and similar catalysts with wide variety of substrates is under progress in our laboratory.

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