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Synthesis of novel metal complexes of lawsone derivative and their applications in CO₂ utilization

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Abstract

A new two fluorescent derivatives of Lawsone have been synthesized and used for CO₂ utilization reactions after complexation with different cations such as Zn²⁺, Fe²⁺ and Ru²⁺. Among the all divalent cations studied receptor molecule La shows increase in absorbance as well as fluorescence towards Zn²⁺ ion. Ligand shows 1:2 stoichiometry of the complex formed between ligand and Zn²⁺, Fe²⁺ and Ru²⁺, which is demonstrated by absorption spectroscopy, elemental analysis and thermo gravimetric analysis. Absorption studies shows better results to explain the role of ligand for selective sensing of Zn²⁺ has been worked out by comparing data with that of control molecule. The complexes of Zn²⁺, Fe²⁺ and Ru²⁺ with ligand have been further studied for utilization of CO₂. Complex synthesized have been tested for carrying out synthesis of N,N-dimethylformamide (DMF) and methyl formate (MF). Catalyst efficiently converts CO₂ into DMF and MF with 42% and 10% yield respectively. Additionally, the catalyst prepared found to be stable in air and can easily be prepared. XRD, TGA, FTIR, and TPD techniques been used to characterized the prepared catalysts.

Keywords: CO₂ utilization, CO₂ reduction Homogeneous catalysis, Hydrogenations CO₂

1. Introduction

2-hydroxy-1,4-naphthoquinone (Lawsone) is naturally occurring compounds (Bot name: lawsonia alba) with reversible valence tautomerism and also shows significant polymorphic behavior^[1, c] which is being used in catalytic, enantioselective addition reaction and biological activities etc. In recent years, due to their redox capacity La is widely being used in range of applications. It also acts as organic radical cofactor for many model compounds. A derivative with amine functionality of it also has immense performance in bio-mimicking synthesis. Transition metal complexes of naphthoquinone derivatives have been played very important role in many biological reactions such as splitting of water molecule by using manganese complexes.^[2, 3]

Transition metals are biologically essential elements and involved in many biological processes.^[4] Zinc is one of the element shows variety of oxidative functions. Similar is the case with iron and ruthenium also involved in many enzymatic reactions.^[5, 6] Mainly Zinc is involved in many biological processes so overload of these results many disorders, so it is necessary to develop economical and simple receptor molecule for selective recognition of Zn²⁺ ion. Derivatives of naphthoquinone are also involved in biological reactions therefore these novel derivatives of lawsone can be synthesized easily with N-O donor functionality. By absorption titration with various concentration of Zn²⁺ cation and ligand were studied in this work.^[7a, 1b] This work is also supported by fluorescence studies.

In CO₂ catalysis mainly hydrogenation these imine based complexes has been worked by many researchers.

Utilization of CO₂ to valuable chemicals is the recent topic for researcher to explore the renewable energy resources. Considering the availability and toxicity CO₂ is widely being used as the sustainable feedstock. Reduction of CO₂ to Dimethyl Formamide and Methyl formate is an attractive route for utilization of CO₂. Various attempts have been made for utilizing carbon dioxide by hydrogenation into formic acids and its derivatives using homogeneous catalyst, an alternative route to the current method in which carbon monoxide used predominantly. Taqui Khan and his collaborators^[7] used [Ru(EDTAH)Cl]- as a catalyst and succeeded in hydrogenation of CO₂ with somewhat large turnover numbers of about 180. Zhaofu Zhan *et al* reported Ionic Liquid (“Si”-(CH₂)₃NH-(CSCH₃)-RuCl₃) for the formic acid production with TOF 103 h⁻¹^[11]. In 1995, P. Jessop, Ikariya and Noyori presented homogeneous catalyst system-RuCl₂(PMe₃)₃ for the hydrogenation of CO₂ to methyl formate^[8]

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with TON 3500 and selectivity of MF 34%. In 2010, Kerry Yu and S. Tsang reported methyl formate synthesis from hydrogenation of CO₂ using copper zinc oxide catalyst^[9] with yield upto 5.67% with respect to methanol.

In the present work we have reported the synthesis of metal-La complex with fluorescent binding studies (cpr ref) and which further being tested as a new homogeneous catalyst for the hydrogenation of CO₂ to DMF and MF.

2. Experimental

2.1 Materials and chemicals

The Hydrogen cylinder was supplied by Vadilal gases and Liquid CO₂ cylinder (99.9%) was procured from De-lux Industrial gases, pune. The double distilled mili-pore de-ionized water was used for the synthesis of the catalysts. Dimethyl amine (35% solution) was supplied by the S.D. Fine chemical Ltd., Mumbai, India, the Metal precursor (>99% assay), KHCO₃ (99.5%), Methanol HPLC grade (>99.5%) were procured from the Merck India, Sodium carbonate (99.5%) was procured from Thomas Backer.

2.2 Catalyst synthesis

2.2.1 Synthesis of receptor molecule i.e. Ligand La:

A Lawsone (2-hydroxy 1,4 naphthoquinone, 1.7 g, 0.1 mol) was dissolved in excess dichloromethane under sonication at 30 °C. Ethanol amine (0.6 mL, 0.1 mol) was added dropwise to above prepared clear solution. The orange red colour solid precipitated out. The reaction mixture was continued for sonication till complete digestion of product. The precipitate was filtered and washed with the same solvent. The product was purified on fast flash column chromatography using pet ether and ethyl acetate as elluents. The Mg-Al-M precursor was prepared using co-precipitation method. For the preparation of HT suitable amount of metal nitrate with Mg:Al:M molar ration of 4:1:0.05 were dissolved in 100 ml of water. Second solution of 0.5 M Na₂CO₃ was prepared and used as precipitation agent. The two solutions were mixed simultaneously with vigorous stirring at room temperature. The mixture was aged for 30 h at 333 K. After filtration the solid cake was washed with water and dried at 353 K. Resulting catalyst was calcinated at 723 K in air for 4 h.

2.2.1 Synthesis of metal complex

Synthesis of ZD: Metal complex of La with zinc acetate was synthesized hydrothermally by 1:2 M: L ratio. The concentration of La was 2 mmol (~0.466 gm) and Zinc acetate (1 mmol, 0.219 g) in aqueous methanol at 80 °C for 6 h. After completion of reaction shiny violet crystals were appeared on cooling then filtered and washed with ether several times.

ZnLa₂OH₂: MW=517.81;

ZnC₂₄H₂₄O₇N₂: C (55.66%), H (4.66%), N (5.40%).

Synthesis of FD: Same procedure of ZLa was followed only with metal salt ferrous sulphate. The Ligand La (2 mmol, 0.466 gm) and Ferrous Sulphate (FeSO₄.7H₂O) (1 mmol, 0.278 g) was dissolved in aqueous methanol. The reaction was carried out hydrothermally at 80 °C for 6 hrs. A black coloured precipitate was obtained. The product was filtered and washed with cold methanol.

FeLa₂OH₂: MW=508.28

FeC₂₄H₂₄O₇N₂: C (56.78%), H (4.75%), N (5.51%).

Synthesis of RD: The reaction of a ligand La (2 mmol, 0.466 gm) and ruthenium trichloride (1 mmol, 0.243 g) in aqueous

methanol was carried out hydrothermally at 80 °C for 8 h. On completion of a reaction black crystals were obtained. The product was filtered, washed with methanol.

RuLa₂Cl₂: MW=606.396;

RuC₂₄H₂₂O₆N₂Cl₂: C(47.53%), H(3.65%), N(4.61%).

2.3 Reaction Procedure

2.3.1 Dimethyl Formamide synthesis

In a typical run, 10 mL (0.07 mol) of 35% Dimethylamine (DMA), 0.078 gm of catalyst, 4.494 mmol KHCO₃, and 100 mL of methanol as solvent were charged and placed in the bomb. The weight of empty bomb and after charging was taken, and then the autoclave was closed tightly and flushed with Hydrogen twice. The autoclave was pressurized to 270 psi with hydrogen and then pressurized with Carbon dioxide using pump until the final pressure comes to 380 psi. The agitator starts with the speed 800 rpm. The reaction mixture was slowly heated to desired temperature, during which the pressure goes up. The reaction temperature was maintained 150 °C for 3h.

The liquid samples were analyzed using an Agilent Technologies 7693 series Gas Chromatography controlled by the open lab control panel software and equipped with an auto sampler unit, by using a Carbowax 20 M capillary column.

2.3.2 Methyl Formate synthesis

In a typical run, 100 ml of methanol and 0.2 gm of catalyst were charged and placed in a bomb. The weight of empty bomb and after charging was taken, and then the autoclave was closed tightly and flushed with hydrogen twice. The autoclave was pressurized to 550 psi (0.306 mol) with hydrogen and then pressurized with carbon dioxide 150 psi (0.083 mol) using pump and the final pressure comes to 700 psi. The agitator starts with the speed 500 rpm. The reaction mixture was slowly heated to 150 °C for 3h. After completion of the reaction, the autoclave was cooled to room temperature and 3h and liquid samples were analyzed further by GC.

3. Results and discussion

3.1 Catalyst characterization¹⁾ Absorption titration studies

The binding studies of receptor molecule ligand La has been shown by absorption spectroscopy. The absorption spectra of ligand shows three absorption maxima at 270 nm, 330 nm, and 460 nm respectively. (Figure 1a) Including one additional band at 250 nm ligand showed increase in absorbance on addition of Zn²⁺ solution selectively. This explains isotopic peak pattern on addition of ligand. (Figure 1b). This has been further confirmed by thermo gravimetric techniques.

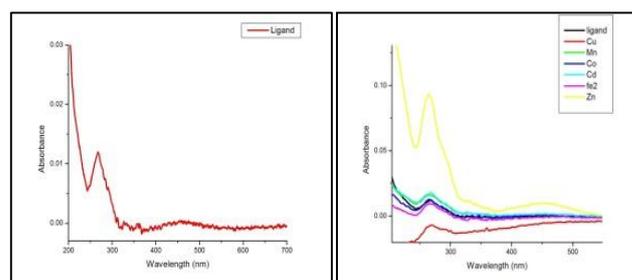


Fig 1: UV-VIS Spectrums of a) Ligand titration with cations b) Zn²⁺, c) Fe²⁺, d) Ru²⁺, e) Ni²⁺, f) Mn²⁺, g) Co²⁺, h) Cu²⁺

Fluorescence studies

Using Water as a solvent, binding abilities of ligand towards M^{2+} has been studied by fluorescence spectroscopy at $10\mu M$ by exciting ligand at 410 nm and recording the emission spectra in the range 420-550nm. The emission maxima observed at 460nm. In fluorescence studies the metal ions used in this study include Zn^{2+} , Fe^{2+} , Ru^{2+} , Cu^{2+} , Mn^{2+} , Ni^{2+} and Co^{2+} . From this for Zn^{2+} fluorescence gets increased on addition of metal ion solution whereas there is no prominent change for other cations which explains non-interactive nature towards ligand.

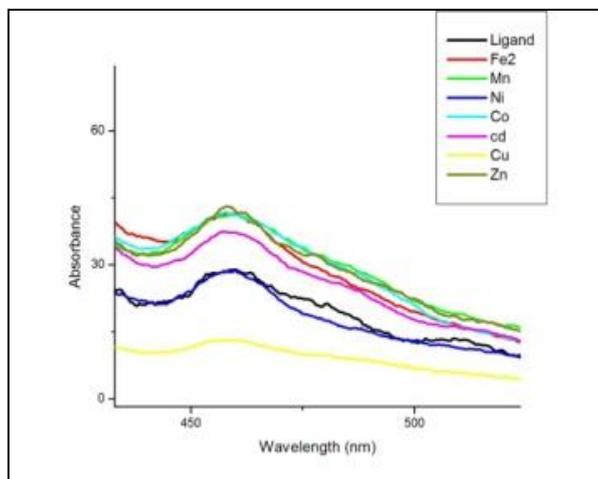


Fig 2: Fluorescence Spectrums of a) Ligand Titration with cation
b) Zn^{2+}

Table 1: TGA study

Compound	Step No.	Temp. Range(°C)	%weight Loss from graph	Probable comp.of group lost	Residue
FD-1	I	74-100	17.2	$2H_2O+0.31L$	FeO
	II	275-500	68.8	1.69L	
ZD-1	I	60-100	29.5	$0.62L+H_2O$	ZnO
	II	320-550	54.3	1.37L	
RD-1	I	150-206	11.0	2Cl	RuO
	II	320-420	28.8	0.5L	
	III	420-600	52.2	1.5L	

3.2 Reaction parametric study

3.2.1 Effect of Metal/ligand variation

Ex	Catalyst	% yield of DMF w.r.t. DMA	% yield of DMF w.r.t. CO_2
1	FD-1	5.8	6.10
2	FL-1	0.4	0.42
3	ZL-1	0.5	0.46
4	RL-1	23.8	25.07
5	RD-1	42.8	42.44

3.2.2 Effect of metal/ ligand on MF formation

4. Conclusion

We have confirmed composition of catalysts using elemental analysis, absorption studies with different cation binding, PL spectra for ligand as well as enhancement with cation, and thermal studies shows best fit for molecular formula given above.

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Thermogravimetric studies

From TGA, the complex FD and ZD complex shows water molecule in coordination sphere as these decomposes around $1000^\circ C$ with two step decomposition (Figure 3). In RD complex three step decomposition explains anhydrous complex and decomposition starts after $150^\circ C$. From the % weight loss the composition of these three complexes has been fitted with elemental analysis. (Table 1) From thermogravimetric analysis FD-1 iron complex shows two step decomposition it confirms aqueous nature of the complex by showing decomposition temperature around $75-80^\circ C$. In second step loss of 1.69 part of ligand with 68.8% weight loss. The residue left after thermogram is iron oxide. Similarly ZD-1 shows two step decomposition with loss of one water molecule in first step also adding loss of 0.62 part of ligand. The % weight loss is 29.5 for this step and which fits the composition. The second step starts at $3200^\circ C$ with loss of 1.38 part of ligand. The residue left after TGA analysis is best fitted for zinc oxide composition. RD-1 shows three step decomposition and it has anhydrous nature from TGA also from IR data. The first step starts at $150^\circ C$ with loss of two chloride ions. The second step starts at $320^\circ C$ with loss of 0.5 part of ligand with weight loss 28.8%. The step three shows 52.2% weight loss with decomposition of 1.5 parts of ligand. The residue left was ruthenium oxide shown in table.

It shows similar behavior with earlier reports of naphthoquinone derivative complexes of iron. ^[1d]

absorbance studies of ligand with different cations and anions.

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