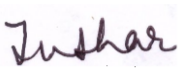
Declaration

I hereby declare that the work presented in this thesis entitled '*Development of Chromium and Molybdenum Complexes for CO_2 Hydrogenation and Biological Application*' submitted to the Indian Institute of Technology Jodhpur in partial fulfilment of the requirements for the award of the degree of Doctor of Philosophy is a Bonafide record of the research work carried out under the supervision of Dr Subrata Chakraborty. The contents of this thesis, in full or in parts, have not been submitted to, and will not be submitted by me to, any other Institute or University in India or abroad for the award of any degree or diploma.

Tushar
P19CY009
30/12/2024



Certificate

This is to certify that the thesis entitled '*Development of Chromium and Molybdenum Complexes for CO_2 Hydrogenation and Biological Application*' submitted by Tushar Singh (P19CY009) to the Indian Institute of Technology Jodhpur for the award of the degree of Doctor of Philosophy, is a bonafide record of the research work done by him under my supervision. To the best of my knowledge, the contents of this report, in full or in parts, have not been submitted to any other Institute or University for the award of any degree or diploma.

Subrata Chakraborty

Dr Subrata Chakraborty
Ph. D. Thesis Supervisor
Date: 31-12-2024

Abstract

The catalytic hydrogenation of the potent greenhouse gas carbon dioxide to value-added products represents a sought-after methodology in academia and industry. Molecular complexes facilitate the conversion of CO_2 into formic acid, which is a beneficial process because formic acid is a versatile feedstock in many industries and can be used as a potential renewable hydrogen storage material. Group VI elements chromium and molybdenum are earth-abundant and low-toxic metals, and their chemistry towards the utilization of CO_2 has been sparsely investigated. Therefore, we examined both the direct and indirect hydrogenation of CO_2 using low-valent Mo(0) and Cr(0) complexes supported by multidentate phosphine ligands with varied bite angles. We achieved maximum formate TONs of 950 and 2,59000, the highest for any Mo and Cr system reported in the literature thus far. Mechanistic probing revealed that the reaction proceeded via the formation of anionic hydride species in both cases. Based on the initial success with low-valent Cr species, we performed CO_2 hydrogenation using high-valent Cr (II) pincer complexes and obtained formate with a TON of 87,00. We also carried out the transfer hydrogenation of CO_2 using isopropanol as the hydrogen source under ambient conditions using bidentate DPPP ligand-based low-valent chromium complex. A formate TON of up to 1974 was recorded using 1 bar CO_2. This is a state-of-the-art discovery with regard to base metal catalysts. Lastly, we developed a NIR II-emitting low-valent Schiff base-supported chromium complex that is effective as an antibacterial agent against gram-positive pathogenic bacteria selectively. The current study deals with transition metal complexes derived from non-noble earth-abundant metals for catalytic and biological applications, and we believe this research opens new avenues for developing next-generation innovative catalysts and bioactive compounds.

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Tushar
Ph.D. Student

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List of Symbols

Symbol	*Description*
μ	Bridging
λ	Wavelength
κ	Kappa
δ	Chemical shift
V	Volume
°	Degree
%	Percentage
d	Interplanar distance
θ	Theta
η	Isobidentate bridging
ν	Frequency
A	Absorbance
I_0	Intensity of incident light
I	Intensity of transmitted light
l	Path length
ϵ	Molar extinction coefficient
c	Concentration
s	Second
h	Hour
τ	Addison's parameter
π	Pi
σ	Sigma
Å	Angstrom
I	Current
mV	Millivolt
mA	Miliampere
eV	Electron volt
1D	One-dimensional
2D	Two-dimensional

List of Abbreviations

Abbreviation	*Full form*
CO_2	Carbon dioxide
DPPM	Bis(diphenylphosphino)methane
DPPE	1,2-Bis(diphenylphosphino)ethane
DPPP	1,3-Bis(diphenylphosphino)propane
DPPF	1,1'-Bis(diphenylphosphino)ferrocene
DiPPF	1,1'- Bis(diisopropylphosphino)ferrocene)
DCPF	1,1'-Bis(dicyclohexylphosphino)ferrocene)
TMEDA	Tetramethylethylenediamine
NHC	N-Heterocyclic Carbene
DNA	Deoxyribonucleic Acid
NIR	Near Infra-red Region
SC-XRD	Single-Crystal X-ray Diffraction
CV	Cyclic Voltammetry
FTIR	Fourier Transform Infra-red
NMR	Nuclear Magnetic Resonance
UV	Ultra Violet
ESI-MS	Electron Spray Ionization Mass Spectrometry
DMF	Dimethylformaide
DMSO	Dimethylsulphoxide
DCM	Dichloromethane
THF	Tetrahydrofuran
OLED	Organic light emitting diode
CIF	Crystallographic information file
TD-DFT	Time-dependent density functional theory
DFT	Density functional theory
HOMO	Highly occupied molecular orbital
LUMO	Lowest Unoccupied molecular orbital
SOMO	Singly occupied molecular orbital
NBO	Natural bonding orbital