Development of Chromium and Molybdenum Complexes for CO_2 Hydrogenation and Biological Application

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Summary and Conclusions

In summary, the thesis focuses on the synthesis and structural characterization of some Chromium and Molybdenum complexes. These complexes were further characterized with ^{1}H, ^{13}C, ^{31}P NMR, FTIR, UV-vis spectroscopy, and ESI-MS spectrometry. These complexes, in parallel with some reported complexes, were explored in the realm of CO2 hydrogenation and in the biological application. The upcoming sections unveil the key highlights of this thesis work.

6.1 SUMMARY

Chapter 1 provides an overview of the Carbon dioxide and carbon dioxide hydrogenation to formate, including literature precedents of various 3d metals and Cr, Mo and W. Furthermore, a snapshot of the biological application of the transition metal complex has also been presented.

Chapter 2 described the Carbon dioxide hydrogenation using various wide bite angle Cr & Mo complexes, which were further extended to bicarbonate and inorganic carbonate hydrogenation. This chapter is further divided into three sections,

Chapter 2(a) described the low-valent Mo complexes bearing bidentate phosphine ligands for CO_2, sodium bicarbonate, and inorganic carbonate hydrogenation to formate. DPPP ligand-supported complex C-3 became the most effective catalyst, producing formate with a maximum TON of 975 in THF/H_2O. This work reports the most efficient non-noble middle transition element Mo catalysts for CO_2 hydrogenation to date. Our studies suggest that the reaction is influenced by the bite angle of phosphine ligands and undergoes an intermediate formato complex formation.

Chapter 2(b) demonstrated low-valent and earth-abundant chromium carbonyl complexes bearing various bidentate phosphine ligands for the hydrogenation of CO_2 to formate. Natural-bite-angle DPPP-supported complex **C-3** exhibited high turnover numbers of up to 259,000 in a THF/H_2O mixture for the formate formation, corresponding to a yield of 60%. Notably, the catalyst was found to be recyclable and bench-stable. Hydrogenation of sodium bicarbonate and inorganic carbonates was also accomplished by employing complex **C-3**. Mechanistic experiments and theoretical studies substantiated that the in situ-generated anionic hydride complex B is the catalytically active species in the hydrogenation reaction. THF and water are crucial in stabilizing the intermediate species in such highly basic reaction conditions.

Chapter 2(c), disclosed the catalytic performance of an earth-abundant chromium pincer complex C-1 in the hydrogenation of CO2 to formate, recording a TON of up to 8700. **C-1** was also explored for sodium bicarbonate hydrogenation to corresponding sodium formate. Mechanistic experiments suggested that the reaction proceeds via a monohydride complex. This work represents the first example of CO_2 hydrogenation using chromium pincer complexes. Further in-depth studies to detect the intermediates are underway in our group. We believe this study will open up avenues for the design of effective pincer chromium complexes for novel bond activation and catalytic reactions.

Chapter 3 delineated earth-abundant, low-valent Cr(0) complexes catalyzed transfer hydrogenation of CO_2 to formate under mild 1 bar pressure without using high-pressure flammable H_2 gas. DPPP ligand-supported chromium complex (C-3) was found to be a very active catalyst and furnishes formate TON with up to 1974 at 1 bar CO2 and 2231 at 5 bar CO2

in the presence of isopropanol as the inexpensive and non-toxic hydrogen source. The catalyst is also active for the hydrogenation of sodium bicarbonate and carbonates to produce their corresponding formates, albeit lower yields were observed. Mechanistic probing indicates that the reaction proceeds via the formation of a hydride complex, which was detected through NMR spectroscopy. This work represents an operationally simple and environmentally benign way to obtain formates via transfer hydrogenation of CO_2 using a base metal catalyst. We believe the state-of-the-art work will inspire the development of novel, homogeneous earth-abundant metal catalysts derived from first-row, non-noble metals for more efficient direct transfer hydrogenation reactions of CO_2 to formate under ambient pressure.

Chapter 4 presented the antibacterial potential of the synthesized chromium-complex **Cr-1** ligand, which was demonstrated with corroboration that this aforementioned ligand potentially kills the Gram-positive bacteria without affecting the Gram-negative one. These results confer the narrow specificity of the chromium-complex **Cr-1** ligand, which can be harnessed to develop new antibacterial agents to combat the infections specifically caused by Gram-positive bacterial pathogens. We extended our investigation to find the potential therapeutic targets of the chromium-complex Cr-1 ligand to establish the probable mode of bactericidal action. Interestingly, in-silico upshots corroborate that this ligand potentially interacts with one of the major drug targets and DNA repair enzyme AP endonuclease. These findings led to the foundations of new drug development in the field of antimicrobial therapy and combating drug-resistant pathogens.

6.2 CONCLUDING REMARKS

Myriads of transition metal complexes have been documented for executing the hydrogenation of carbon dioxide to formate. However, reports on Cr & Mo complexes were scarce, and reported catalysts displayed inferior activity, accordingly, which provides room to investigate this domain further. The current thesis explores the synthesis of some novel Cr(0) bite angle complexes, which, along with some other known bite angle complexes of Cr & Mo, have been explored in the hydrogenation of CO2, sodium bicarbonate and fewer carbonates to get formate as a product. A high TON of 2,59000 was observed in the case of Cr, while a TON of 975 was recorded with Molybdenum complexes. Hydrogenation of CO_2 and sodium bicarbonate to formate was also achieved using Cr(II) pincer complexes with the highest TON of 8700. We have also documented the transfer hydrogenation of Carbon dioxide to formate using Cr bite angle complexes as catalysts under ambient pressure of 1 bar CO2 with a TON of 1974 and 2231 using 5 bar pressure utilizing Isopropanol as a hydride source. This is a state-of-the-art discovery with regard to the base metal catalysts. Lastly, we synthesized a novel Schiff base supported low-valent Cr complex and explored its activity as a potential antibacterial agent against gram-positive bacteria. We believe that the arena of homogeneous catalysts using Cr and Mo complexes will continue to rise, as described in the thesis, as a potential catalyst in carbon dioxide hydrogenation and transfer hydrogenation to formate. It will help the readers to explore further Cr & Mo complexes in the repertoire of CO_2 utilization. We believe that more potential anti-bacterial agents based on Cr complexes will also appear in coming years.

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