

# The Design Aspects of Metal Complexes in CO<sub>2</sub> Reduction: A Mini Review

Nyasha Makuve  
PhD University of Johannesburg

**Abstract:- Catalytic hydrogenation of carbon dioxide to value-added chemicals is an attractive process to address both energy and environmental issues. Several approaches have been used to convert the greenhouse gas to useful products. This conversion has been done mainly through homogeneous catalysis using rhodium and ruthenium complexes. In recent years there has been a growing concern to design catalysts that are able to convert carbon dioxide to C1 products. Several approaches such as electrochemical and photochemical reduction of carbon dioxide using metal complexes has been studied. Results from these studies indicate that metal complexes may answer both environmental and energy issues associated with the production of the greenhouse gas. This contribution will focus on the recent development in the design and application of metal complexes in catalytic hydrogenation of carbon dioxide.**

**Keywords:- Carbon Dioxide, Metal Complexes Design, Electrochemical and Photochemical Reduction.**

## I. INTRODUCTION

Awareness, strategies and technologies associated with the high levels atmospheric carbon dioxide (CO<sub>2</sub>) has been a major concern in the field of environmental protection and sustainable development.<sup>1,2</sup> Recycling of CO<sub>2</sub> into value-added chemicals, CO<sub>2</sub> fixation and conversion have been hot topics since CO<sub>2</sub> is a sustainable C<sub>1</sub> resource.<sup>3,4</sup> The utilisation of CO<sub>2</sub> through catalytic processes such as hydrogenation, amidation and carboxylation has been a major concern due to the ever-increasing CO<sub>2</sub> levels in the atmosphere.<sup>5,6</sup> The chemical inertness and thermodynamic stability of CO<sub>2</sub> makes these processes to be challenging bringing about the expansion of this area of study.<sup>7</sup> This has led to the development of catalysts that can aid in the mitigation of atmospheric CO<sub>2</sub> by adsorbing and activating CO<sub>2</sub> efficiently. The large-scale implementation and deployment of all these processes requires low cost and selective catalysts for CO<sub>2</sub> reduction over the competing H<sub>2</sub> evolution reaction. Heterogeneous transition metal catalyst<sup>8</sup> and homogenous catalyst has been explored in the reduction of CO<sub>2</sub> with homogeneous catalyst being advantageous due to the direct catalyst performance analysis and ligand design. The use of only earth abundant metal (Fe, Cu, Mn, Ni, Co) complexes in electrochemical and photochemical reduction have been of great use due to cheap electrodes, visible light sensitizers and cheap sacrificial electron donor.<sup>9,10</sup> This

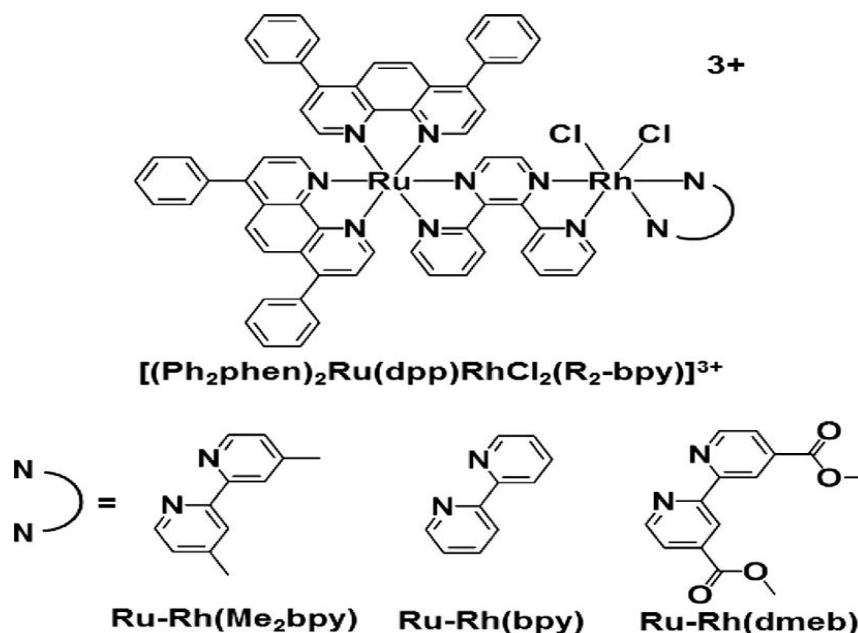
brings us to the focus of this review, which is the design aspects of metal complexes applied in CO<sub>2</sub> reduction. However, a review on bonding nodes and synthetic methods of complexes for CO<sub>2</sub> reduction was recently covered by Parapo and Okuda.<sup>11</sup>

## II. METAL COMPLEXES FOR CATALYTIC REDUCTION OF CO<sub>2</sub>

Catalytic hydrogenation of CO<sub>2</sub> has attracted a lot of attention in the designing of effective and selective catalyst due to the attractive products of the catalytic reactions. A variety of ligands and complexes have been synthesised with the quest of finding the best catalyst with the highest selectivity. One of the low-cost metals that have attracted attention in catalytic hydrogenation of CO<sub>2</sub> is manganese. Computational studies on manganese based complexes by Rawat and co-workers revealed that carbonyl (CO)  $\pi$ -acceptor ligands role is to favour the heterolytic H<sub>2</sub> cleavage and the role of  $\delta$ -donor ligands such as PH<sub>3</sub> is to favour hydride transfer during the hydrogenation process.<sup>27</sup>

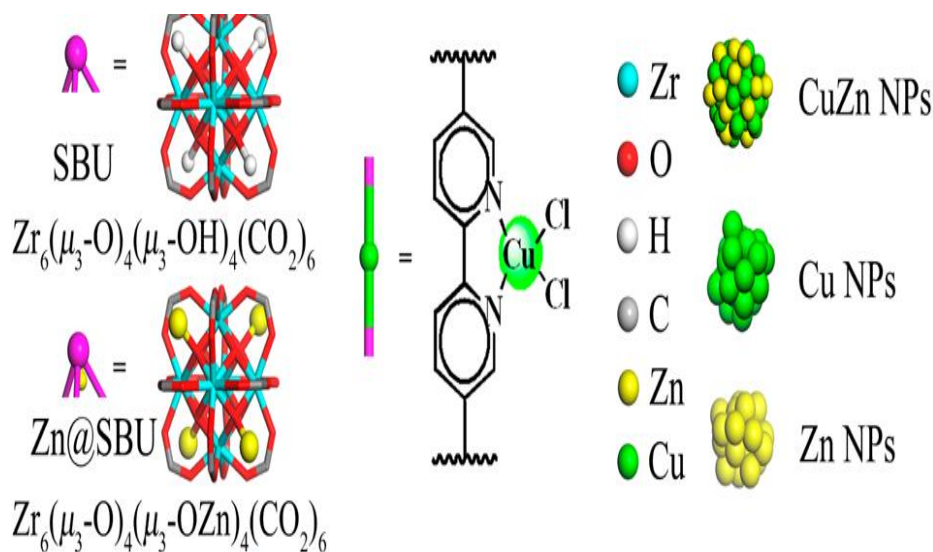
Ge and co-workers computational studies on Co complexes containing acylmethylpyridinol ligand also revealed that the acylmethylpyridinol ligand assist in the cleavage of H<sub>2</sub> by forming strong Co-H <sup>$\delta^-$</sup> ...H <sup>$\delta^+$</sup> -O dihydrogen bond with a total free energy barriers for the hydrogenation of CO<sub>2</sub> and dehydrogenation of formic acid as low as 23.1 kcal/mol in water.<sup>28</sup> The hydrogen bonding was in a Lewis pairs fashion<sup>29</sup> with density functional theory calculations indicating the energy barriers. Frustrated Lewis pairs (FLPs) formed from the combination of Lewis acids and other ligands such as phosphines in the presence of metals such as aluminium continue to attract attention in the hydrogenation of CO<sub>2</sub> to methanol because (FLPs) can easily bind to CO<sub>2</sub> and easily react with effectively with small molecules.<sup>30</sup> The combination of the Lewis acid and Lewis base to form (FLPs) brings about these favourable conditions because of their restricted geometric and steric interactions.<sup>31</sup>

Bipyridyl complexes of Ru(II), Iridium,<sup>12</sup> Rh(III)<sup>13</sup> and Re(II)<sup>14</sup> have been employed in the reduction of CO<sub>2</sub> due to their high CO<sub>2</sub> surface concentration, affinity for CO<sub>2</sub> binding, ability to inhibit dimerization and in some cases redox noninnocence of the bipyridyl ligand. The high turnover rate and high selectivity of CO<sub>2</sub> conversion during catalytic cycles is due to the chemical bond between CO<sub>2</sub> and the metal centre.



**Figure 1:** New Ru(II), Rh(III) bimetallic complexes of  $[(\text{Ph}_2\text{phen})\text{Ru}(\text{dpp})\text{RhCl}_2(\text{R}_2\text{-bpy})](\text{PF}_6)_3$  complexes ( $\text{R} = \text{CH}_3$ ,  $\text{H}$ , or  $\text{COOCH}_3$ ;  $\text{dpp} = 2,3\text{-bis}(2\text{-pyridyl})\text{pyrazine}$ ;  $\text{dpy} = 2,2$  bipyridine;  $\text{dmeb} = 4,4'$ -dimethyl ester- $2,2'$ -pyridine.)<sup>13</sup>

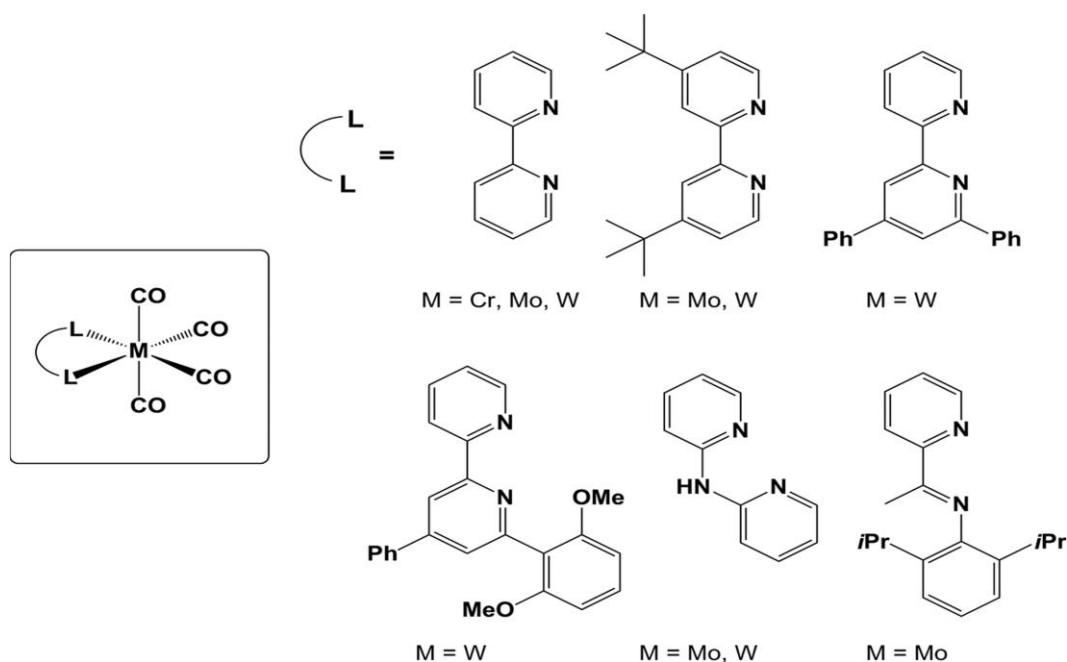
2,2'-bipyridine-5,5'-dicarboxylate bridging ligands have been used as platform molecules for the synthesis of Cu/ZnO and Cu/ZrO<sub>2</sub> metal organic frameworks (MOFs) which were effective catalyst for the catalytic hydrogenation of CO<sub>2</sub> to methanol with 100 % selectivity.<sup>15</sup> The activity had a space-time yield of up to 2.59 g<sub>MeOH</sub> kg<sub>Cu</sub><sup>-1</sup> h<sup>-1</sup>. Manganese complexes with *m*-terphenyl isocyanide ligands have shown to improve kinetic stability during CO<sub>2</sub> reduction.<sup>16</sup> Oxalate ligands have attracted less attention in the utilisation of CO<sub>2</sub> into methanol and methyl formate because of their instability in solution.<sup>17</sup>



**Figure 2:** Bipyridine ligand for MOFs synthesis.<sup>15</sup>

## 2.1. Metal Complexes for Electrocatalytic Reduction of CO<sub>2</sub>

The electrocatalytic reduction of CO<sub>2</sub> to various commodity chemicals and fuels has utilised sophisticated ligands of phosphines, diimines,<sup>18</sup> porphyrins, phthalocyanines and some pyridine ligands cooperated with metal carbonyl species<sup>19</sup> just to mention a few. Homogeneous electro-catalysts have gained much attention due to their advantages of using renewable energy sources including solar energy, ability to be controlled and analysed by a variety of analytical techniques. Metals available naturally and able to convert CO<sub>2</sub> especially group 6 metals such as molybdenum have been utilised in electrocatalytic reduction of CO<sub>2</sub>.<sup>20</sup>



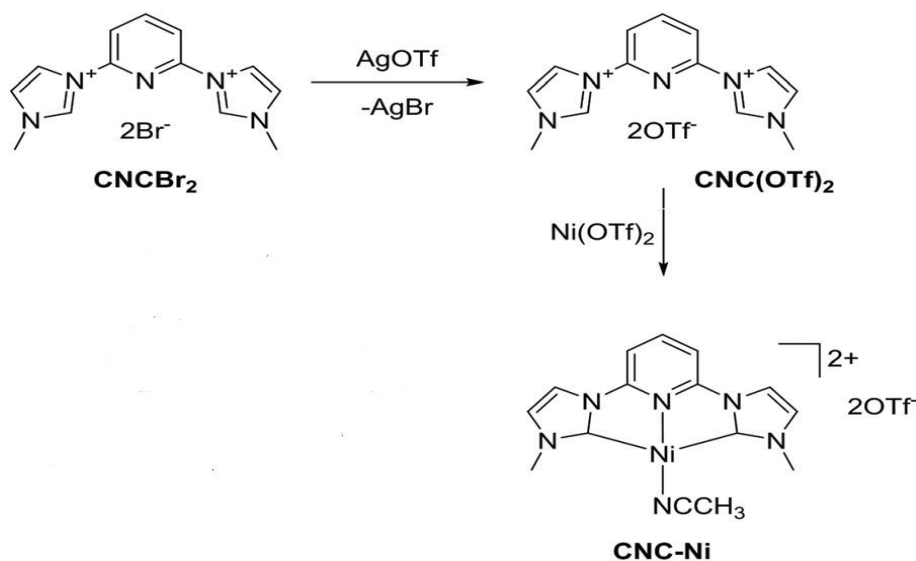
**Figure 3:** Ligands used for the synthesis of  $M(L)(CO)_4$  species for  $CO_2$  reduction.<sup>20</sup>

### III. CHALLENGES ASSOCIATED WITH $CO_2$ ELECTROCATALYTIC REDUCTION.

In electrocatalytic reduction of  $CO_2$ , the two-proton reduction of  $CO_2$  to carbon monoxide (CO) in the presence of bipyridine metal catalyst<sup>21</sup> is a possible way of forming alternative fuels but it is governed by the thermodynamic potential of the  $CO_2$  reduction to CO which is  $-0.53$  V *versus* standard hydrogen electrode (SHE). In the presence of a proton donor such as  $H_2O$ , the reaction will favour the  $H_2$  evolution reaction (HER) which has a less negative potential of  $-0.413$  V *versus* SHE. The designing of catalysts with higher selectivity of HER in the presence of proton donors lowers Faradaic efficiency and also divert reducing power of proton donor thus achieve the desired reduction products. This challenge was addressed by Sheng and co-workers who synthesised a pyridyl-biscarbene tridentate diamagnetic

nickel pincer complex with a pseudo square planar geometry which had a high selectivity for electrocatalytic reduction of  $CO_2$  over  $H_2O$  and the reaction was monitored by cyclic voltammetry and ultra violet –visible spectrometry.<sup>22</sup>

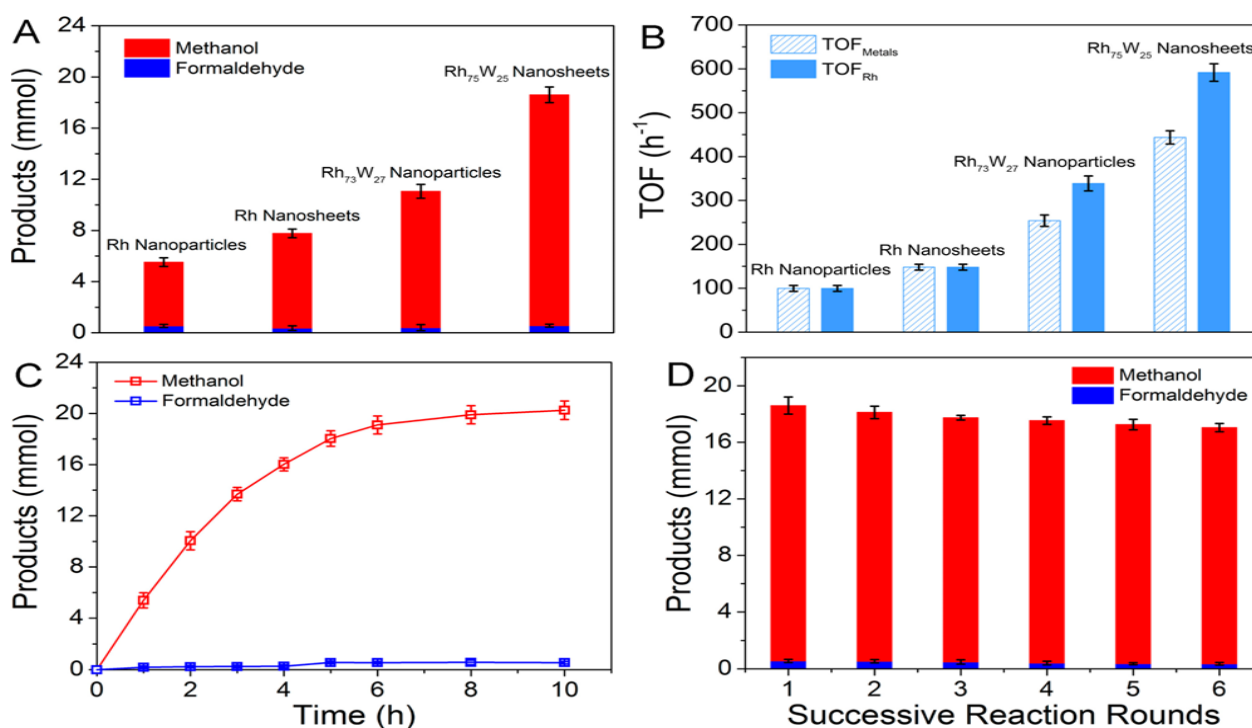
In electrocatalysis, an additional pathway is required to activate the molecular catalyst that requires a negative potential to achieve the catalytic reduction of  $CO_2$ . Even after finding the pathway, the molecular catalysts tend to dissolve and undergo dimerism during a long-term catalytic cycle that leads to low conversion of  $CO_2$  to desired products such as methanol and formic acid. A combination of the molecular catalyst and a semiconductor can solve the problem, but these systems require high overpotential, low Faradaic efficiency and low selectivity towards required products such as formic acid.



**Figure 4:** Synthetic scheme of a planar nickel-CNC pincer complex which exhibits high selectivity for electrocatalytic reduction of  $CO_2$ .<sup>22</sup>

The adsorption and activation of CO<sub>2</sub> on catalyst surface is depended on d-band centre and surface negative charge. This is one of the critical areas for successful CO<sub>2</sub> hydrogenation. Tuning catalyst dimensions and alloying with non-noble metals can utilised as a way of engineering or modelling d-band centre and negative charge density of the metal catalyst thus improving catalytic activity. Tuning catalyst dimension gives a platform for effective modulation of electronic properties by variation of the spatial distribution of electrons whilst alloying induces the charge transfer between different metals thus varying charge distribution on the surface. This strategy promotes CO<sub>2</sub>

activation to CO<sub>2</sub><sup>δ-</sup> at the region with high negative charge density and the adsorption of intermediates to be further hydrogenated to methanol. Zhang and co-workers synthesised and fully characterised a range of Rh-based nanocrystals including Rh<sub>75</sub>W<sub>25</sub> nanosheets based on the alloy effect and integration of quantum confinement for the effective and improved CO<sub>2</sub> hydrogenation.<sup>23</sup> Rh<sub>75</sub>W<sub>25</sub> nanosheets had a high turnover frequency (TOF) number of 592 h<sup>-1</sup> that was 5.9, 4.0 and 1.7 times higher than that of Rh nanoparticles, Rh nanosheets and Rh<sub>73</sub>W<sub>27</sub> nanoparticles. The obtained results clearly prove the importance combining the two strategies to tune electronic properties.



**Figure 5:** (A) CO<sub>2</sub> hydrogenation products over Rh nanoparticles, Rh nanosheets, Rh<sub>73</sub>W<sub>27</sub> nanoparticles, and Rh<sub>75</sub>W<sub>25</sub> nanosheets at 150 °C after 5 h. (B) TOF<sub>metals</sub> and TOF<sub>Rh</sub> catalyst comparison. (C) CO<sub>2</sub> hydrogenation catalysed by Rh<sub>75</sub>W<sub>25</sub> nanosheets at 150 °C time course. (D) Rh<sub>75</sub>W<sub>25</sub> nanosheets relative activity and selectivity over a course of 6 rounds of successive reaction with error bars representing standard deviation from three independent measurements.<sup>23</sup>

### 3.1 Challenges Associated with CO<sub>2</sub> Photocatalytic reduction.

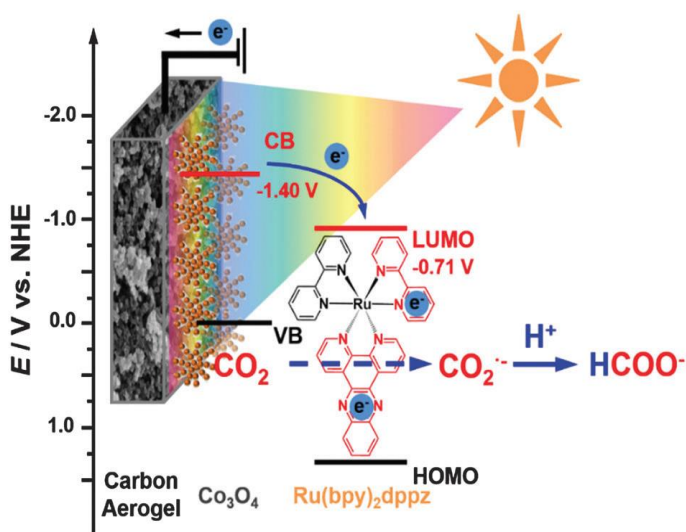
The adsorption of CO<sub>2</sub> on photocatalysts surface is the most crucial stage in CO<sub>2</sub> photocatalytic reduction. This stage is a pseudo-first-order reaction since CO<sub>2</sub> photo-reduction increase with the initial CO<sub>2</sub> concentration. However, the kinetics of CO<sub>2</sub> photocatalytic reduction depends on many factors such as CO<sub>2</sub> activation,  $e^-h^+$  recombination, catalyst illumination,<sup>24</sup> reactant adsorption, product desorption, incident light intensity and fraction, specific area, surface and crystalline properties of photocatalysts.<sup>25</sup> These factors have led to the development of photocatalysts that can improve selectivity, productivity and rate of reaction.

To overcome these problems one of the approaches is the use of semiconductors with wide band gap energies in the design of photocatalysts to provide sufficient positive redox and negative potentials in valence bands and conduction bands respectively. The major drawback of this

approach is the use of high-energy input. The incorporation of narrow band gap energies semiconductors in the design of photocatalysts is not conducive because of catalyst decomposition due the hole formation and they only work in the visible range.

Favourable approaches include the use of two or more semiconductor composites, doping with non-metals and metal particles doping. These approaches increase charge separation and photocatalytic reduction efficiency. The combination of photocatalysts and electrocatalysts can be utilised to provide a lowpotential CO<sub>2</sub> reduction. Huang and co-workers ventured into this study whereby porous adsorption carbon aerogel, robust visible-light harvester Co<sub>3</sub>O<sub>4</sub> (photocatalyst) and Ru(II)bipyridyl complexes as molecular catalyst were combined for formate production from CO<sub>2</sub> reduction.<sup>26</sup> The results obtained were favourable considering that CO<sub>2</sub> conversion to formate occurred at an onset potential of -0.45 V (vs .normal hydrogen electrode) under photoelectrochemical conditions with a selectivity of

formate at 99.95 % upon applying potential of -0.60 V (vs .normal hydrogen electrode) with a production rate of about  $110 \mu\text{mol cm}^{-2} \text{h}^{-1}$  and Faradaic efficiency of 86 %. The conversion had an electron transfer rate of  $2.94 \times 10^{-3} \text{ cm}^{-1} \text{ s}^{-1}$ .



**Scheme 1:** Plots of CO<sub>2</sub> adsorption-enhanced Ru(bpy)<sub>2</sub>dppz-Co<sub>3</sub>O<sub>4</sub>/Carbon Aerogel interface together with its energy level diagram.<sup>26</sup>

#### IV. CONCLUSION AND PERSPECTIVE

Carbon dioxide as a major greenhouse gas with increased concentration in the atmosphere is being considered responsible for the global warming and climate changes. Its conversion into fuels and chemicals offer opportunities to mitigate the increasing build up. The present study has analysed the current status of metal complex designs as candidates for catalytic hydrogenation of CO<sub>2</sub>. This mini review has covered a number of metal complex (pre)catalysts for CO<sub>2</sub> hydrogenation such as photocatalytic reduction, electrocatalytic reduction and catalytic reduction by hydrogen. These technologies are still in research but are potential candidates for mitigating the still increasing atmospheric CO<sub>2</sub> concentrations. Based on abundant reported examples metal complexes are good homogenous catalysts for catalytic hydrogenation of CO<sub>2</sub> under various conditions.

#### REFERENCES

- [1]. W. Wang, S. Wang, X. Ma and J. Gong, *Chem. Soc. Rev.*, 2011, **40**, 3703–27.
- [2]. J. Albo, P. Castaño and A. Irabien, *Green Chem.*, 2013, 1–3.
- [3]. Q. Liu, L. Wu, R. Jackstell and M. Beller, *Nat. Commun.*, 2015, **6**, 1–15.
- [4]. Y. Li, X. Cui, K. Dong, K. Junge and M. Beller, *ACS Catal.*, 2017, **7**, 1077–1086.
- [5]. E. Alper and O. Y. Orhan, *Petroleum*, 2017, 1–8.
- [6]. Sekizawa, Keita, Maeda, Kazuhiko, Domen, Kazunari,

Koike, Kazuhide, Ishitani, Osamu, *J. Am. Chem. Soc.*, 2013, **135**, 4596–4599.

- [7]. C. Thibault, Cantat and Chauvier, *ACS Catal.*, 2017, **7**, 2107–2115.
- [8]. S. Das, S. Biswas, T. Balaraju and S. Barman, *J. Mater. Chem. A Mater. energy Sustain.*, 2016, **4**, 8875–8887.
- [9]. H. Takeda, C. Cometto, O. Ishitani and M. Robert, *ACS Catal.*, 2017, **7**, 70–88.
- [10]. A. Abdelwahab, J. Castelo-quibén, M. Pérez-cadenas and A. F. Pérez-cadenas, *Catalysts*, 2017, **7**, 25.
- [11]. A. Paparo and J. Okuda, *Coord. Chem. Rev.*, 2017, **334**, 136–149.
- [12]. P. Kang, T. J. Meyer and M. Brookhart, *Chem. Sci.*, 2013, **4**, 3497–3502.
- [13]. H. J. Sayre, T. A. White and K. J. Brewer, *Inorganica Chim. Acta*, 2017, **454**, 89–96.
- [14]. X. Qiao, Q. Li, R. N. Schaugaard, B. W. No, Y. Liu, D. Li, L. Liu, K. Raghavachari and L. Li, *J. Am. Chem. Soc.*, 2016, 1–4.
- [15]. B. An, J. Zhang, K. Cheng, P. Ji, C. Wang and W. Lin, *J. Am. Chem. Soc.*, 2017, **139**, 3834–3840.
- [16]. D. W. Agnew, M. D. Sampson, C. E. Moore, A. L. Rheingold, P. Kubiak and J. S. Figueroa, *Inorg. Chem.*, 2016, **55**, 12400–12408.
- [17]. O. Bolarinwa, S. Faiz, H. Tasfy, N. Asmawati and M. Zabidi, *Biochem. Pharmacol.*, 2017, **17**, 273–283.
- [18]. Q. Zeng and J. Tory, *Organomet. Chem.*, 2014, **3**, 5002–5008.
- [19]. C. W. Machan, *Dalt. Trans.*, 2016, **45**, 17179–17186.
- [20]. K. A. Grice and C. Saucedo, *Inorg. Chem.*, 2016, **55**, 6240–6246.
- [21]. M. Daryanavard, H. Hadadzadeh, M. Weil and H. Farrokhpour, *Biochem. Pharmacol.*, 2017, **17**, 80–89.
- [22]. M. Sheng, N. Jiang, S. Gustafson, B. You, D. H. Ess and Y. Sun, *Dalt. Trans.*, 2015, **44**, 16247–16250.
- [23]. W. Zhang, L. Wang, H. Liu, Y. Hao, H. Li, M. U. Khan and J. Zeng, *ACS Nano Lett.*, 2017, **17**, 788–793.
- [24]. X. Zhang, X. Li, D. Zhang, N. Q. Su, W. Yang, H. O. Everitt and J. Liu, *Nat. Publ. Gr.*, 2017, **8**, 1–9.
- [25]. W. Wang, J. Soulis, Y. J. Yang and P. Biswas, *Aerosol Air Qual. Res.*, 2014, **14**, 533–549.
- [26]. X. Huang, Q. Shen, J. Liu and G. Zhao, *Energy Environ. Sci.*, 2016, **9**, 3161–3171.
- [27]. K. S. Rawat, A. Mahata and B. Pathak, *J. Phys. Chem.*, 2016, **120**, 26652–26662.
- [28]. H. Ge, Y. Jing and X. Yang, *Inorg. Chem.*, 2016, **55**, 12179–12184.
- [29]. F. Fontaine, M. Courtemanche, M. Légaré and É. Rochette, *Coord. Chem. Rev.*, 2017, **334**, 124–135.
- [30]. N. C. Smythe, D. A. Dixon, E. B. Garner, M. M. Rickard, M. Mendéz, B. L. Scott, B. Zelenay and A. D. Sutton, *Inorg. Chem. Commun.*, 2015, **61**, 207–209.
- [31]. Y. Zhang, P. G. Williard and W. H. Bernskoetter, *Organometallics*, 2016, **35**, 860–865.