CH039 – 2 Page Summary

N-heterocyclic carbenes (NHCs) are possible metal catalysts that are able to overcome the kinetic barriers. Carbenes have the ability to attach themselves to metals to form metal-carbene complexes[i]. As efficient catalysts, carbenes are potential molecules that are applied in several of the engineering faculties such as material science and harnessing of energy.

This research features N-heterocyclic carbenes (NHCs), which are well known for their organocatalysys nature and ligands in organic synthesis. NHCs have the ability to stabilize and activate metal centres in organic syntheses[ii]. In addition, the availability of two valence electrons allow Fischer N-heterocyclic carbene to act as nucleophliles, giving rise to the possibility of bonding them together with other anions to form complexes. Previous research has shown that nucleophilic NHCs have the ability to activate CO_2 to form imidazolium carboxylates, making it highly applicable in industries. However, application of the imidazolium carboxylates formed from the activation of CO_2 is highly limited by the preparation of precursors to NHC–metal complexes and halogen-free ionic liquids, and some stoichiometric transcarboxylation reactions[iii]. In this project, chromium is used as metal center for carbene ligands due to its relatively lower price compared to palladium or ruthenium and hence, its feasibility in being used in industry[iv]. Nonetheless, despite the high costs of the reducing agent, imidazolium salt, we will be making use of it in our experiment. In this work, we envision to reduce carbon dioxide using Group VIB transition metal-NHC as catalyst with a higher yield. We also aim to investigate the catalytic activity of metal-NHC in the reduction of CO_2 through practical and computational analysis. We hypothesize that group VIB metal N-heterocyclic carbenes are able to catalyse the reduction of CO_2. Among Cr, Mo and W, there exists a trend as the size of atoms increases. W (Tungsten) will have greatest efficiency in catalytic process as it has more space for ligands to bond to. We also conjecture that theoretically, the presence of metal NHC will facilitate the reaction by lowering the activation energy.

The synthesis yields of different metal-NHCs are determined from Infrared Spectrum. A peak at 1100cm^{-1} is used as the reference peak. An obvious shift occurs at the 1900-2100cm^{-1} zone, which characterises C≡O bond. A coordinative bond between the metal center and the 1,3- diisopropyl imidazolium ion must have affected the backbonding of the metal and thus, shifted the peak to the left in the case of Cr-NHC. This increase in wavenumber at the region of C≡O stretch of the CO group which bonds with Cr center implies a decrease in backbonding from the carbene that is now attached. On the other hand, for Mo, the shift around 1900-2100cm^{-1} zone is to the right, which means there is decrease in wavenumber at the C≡O stretch. This implies that backbonding from the carbene to the Mo center increases, which might hinder the catalytic activity of the N-heterocyclic carbene during reaction.

The yield of Mo-NHC is relatively lower than that of Cr-NHC and W-NHC, probably due to the lower solubility of $Mo(CO)_6$ in THF solvent.

After one hour, Cr-NHC synthesized from 1,3- diisopropyl imidazolium chloride showed greatest activity in the reduction of CO_2. The rate of decrease in volume of CO_2 is highest when Cr-NHC is the catalyst, followed by Mo-NHC and W-NHC. Carbenes synthesized from 1,3- diisopropyl imidazolium chloride also seems relatively more efficient as catalysts compared to carbenes synthesized from 1 – ethyl – 3- methyl imidazolium bromide.

Given that CO_2 is the most unreactive compound in the reaction mixture, it is likely that the crucial step lies in the activation of CO_2 by forming imidazolium carboxylate. This process requires the coordinate bond between the metal center and the imidazolium ligand to be broken, thus activation energy of the reaction might be higher compared to the case of free N-heterocyclic carbene as catalyst. The next step is the formation of a key intermediate, formoxylane, that can further react with the reducing reagents (triethylsilane) to possibly form other compounds that can be further hydrolysed into methanol and CO[v].

Attempts to isolate the imidazolium carboxylate as well as formoxylate intermediate were unsuccessful as they are unstable. A possible way to increase the stability of the intermediates is to introduce bulky substitute groups such as phenyl group.

Calculations were performed to further explain the experimental results that we have obtained. The formation

energy of the various metal-carbene pentacarbonyl complexes was calculated as follows: $E_f = (E_{complex} + E_{CO}) - (E_{hexacarbonyl} + E_{free\ carbene})$
The energy of the starting metal carbonyls do not follow the trend Cr < Mo < W. This can be explained by the previous researches that have shown that besides the conventional d_π -> 2π donor-acceptor (DA) bonding, there is another DA interaction between the d-orbital resulted from the three-centre hyperbond (3CHB) hyperconjugation[vivii]. $Cr(CO)_6$, as compared to $Mo(CO)_6$ and $W(CO)_6$, has higher energy due to the unusually high back-donation. Due to the presence of Cr, Cr carbene also experiences this high back-donation, resulting in the greatest energy change. As we can see from the total energy changes, it can be expected that the reaction between Cr carbonyl and the free carbene (-0.5309eV) will result in the greatest yield, followed by Mo (-0.1123eV) and lastly, W (0.0247eV). This draws correspondence to our practical experiments, which has the same outcome.

The Climbing Image Nudged Elastic Band Method[viii], with a force convergence threshold of 0.05 eV/A, was used to calculate the transition state complex, and the activation energy of both the catalysed and uncatalysed hydrosilylation of CO_2. Broyden dynamics was used to aid convergence.

Computation calculations via the aforementioned method show that the activation energy of the reaction is relatively high without the catalyst (~0.4eV). With the metal carbene catalyst, the activation energy is significantly reduced. According to the simulation conducted, it is evident that the main energy barrier is caused by the formation of the triethysilane-carbon dioxide complex (at time period 8). This can be further supported by the investigation of the relative changes in charges of the atoms involved in the formation of the intermediate. It is found that Si atom from triethylsilane, C and O atoms from carbon dioxide are the main atoms involved. As seen from the figure below, there is a great dip in charge for Si atom (39.671eV to 36.297eV) coupled by the relative surge in charge of O atom (61.843eV to 61.345eV) and small increase in charge of C atom (87.967eV to 89.207eV) between time periods 8 and 9. The aforementioned changes in charges denote the formation of the complex in which charges are being shared between the atoms. It can thus be hypothesized from the simulation that the presence of metal carbene acts as a catalyst by providing an alternative mechanism involving a transition state so as to lower the activation energy. This reduced the energy barrier that would otherwise slow the reaction down.

Our hypothesis is partially true as Group VIB metal NHC significantly facilitates the reduction of CO_2. This conclusion is further supported by computational analysis as theoretically, activation energy in the reduction of CO_2 is significantly reduced with the presence of Metal NHC. However, the trend that we predicted is not totally accurate. For carbenes generated from 1,3- diisopropyl imidazolium chloride, the reactivity of catalysts decreases as we go down group VIB. However, for carbenes generated from 1 – ethyl – 3- methyl imidazolium bromide, Mo-NHC is more reactive as catalyst. We have proposed a mechanism of the reduction of CO_2. However, more research can be done to confirm this mechanism by verifying the existence of the intermediates. The attached group in imidazolium salts can also be varied to investigate the effects of different substituents on the properties of metal carbene. Further research should also characterise the reduction of CO_2 by finding the most suitable reducing reagents or reaction conditions so as to achieve highest possible yield of methanol from CO_2.

---

[i] NO AUTHOR.2009. http://www.physorg.com/news175440301.html
[ii] Wolfgang A. Herrmann,2002
[iii] Siti Nurhanna Riduan, Yugen Zhang, and Jackie Y. Ying, 2009
[iv] Aldo Bonincontro.2008. Retrieved from http://www.helium.com/items/1234895-the-main-chemical-properties-of-chromium
[v] Yugen Zhang, Siti Nurhana Riduan and Jackie Y.Ying, Angew. Chem. 2009, 121, 3372-3375
[vi] Wang, S.P.; Yan, K.M.; Hsu, W.Y. *J. Chin. Chem. Soc.* **2009,** 56, 1205-1215.
[vii] G. Henkelman, B. P. Uberuaga, and H. Jonsson, The Journal of Chemical Physics, **113**, 9901 (2000)
[viii] G. Henkelman, and H. Jonsson, The Journal of Chemical Physics, **113**, 9978 (2000)