EXTENDED ABSTRACT

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Theoretical study on co2 reduction mediated by ru-pincer complexes: an implication towards efficient catalyst design

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Abstract:

Carbon dioxide is not only found to be economical and renewable carbon source but also serves as important C1 building block for many chemicals. Besides contributing in the sustainable development of chemical industry these products like formic acid or methanol also behave as potential hydrogen storage agents. As such, hydrogenation of CO2 has grabbed immense interest of researchers and its efficient conversion has turned out to be a subject of numerous studies. Few noble first row transition metals viz. Fe and Co have been used in homogenous systems to catalyse the reaction, however recent reports also include metals like Rh, Ir, Ru. Nozaki and co workers introduced an Ir based PNP complex for CO2 hydrogenation which involved a complex mechanism in which ligand dearomatization was a major step. Later on, theoretical reports of Yang and Ahlquist confirmed that base assisted mechanism was energetically more favourable. The use of Ru-PNP and PNN complexes in recent times is worth mentioning. These complexes reversibly bind CO2 forming 1,3-CO2 adducts. Huff and Sanford used PNN pincer ligands and reported a TOF of 2200 h-1. Filonenkoet. al showed that metal-ligand cooperation in Ru-PNP complexes lowers the efficiency of the catalytic reaction. Although there exist a few theoretical reports on the mechanism of CO2 hydrogenation to formates, but a detailed investigation with thorough discussions on various steps generating different intermediates is rare. This has prompted us to design new Ru-catalysts by modifying the PNP framework of the ligand (1a, 1b and 1c) and study its effect on the energetics of the reaction. In addition, DFT calculations are performed to illustrate the estimate effect of replacing the substituents at P-atom with electron donating (Me) and electron withdrawing groups (F).

Introduction:

Ankur K Guha has completed his at the age of 28 years from Tezpur University, Assam, INDIA. After a post doctoral stay with Prof. S. R. Gadre of IIT Kanpur, he joined the department of Chemistry, Cotton University, Assam, INDIA, as an assistant professor in the year 2015. His research interest includes reaction mechanism, structure and bonding and theoretical spectroscopy. He has over 60 publications that have been cited over 500 times, and his publication H-index is 14.

Carbon dioxide is one of the end products of combustion, and is not a benign component of the atmosphere. The concentration of CO2 in the atmosphere has reached unprecedented levels and continues to increase owing to an escalating rate of fossil fuel combustion, causing concern about climate change and rising sea levels.1-6 In view of the inevitable depletion of fossil fuels, a possible solution to this problem is the recycling of carbon dioxide, possibly captured at its point of generation, to fuels.5,7-12 Researchers in this field are using solar energy for CO2 activation and utilization in several ways: (i) so-called artificial photosynthesis using photo-induced electrons; (ii) bulk electrolysis of a CO2 saturated solution using electricity produced by photovoltaics; (iii) CO2 hydrogenation using solar-produced H2; and (iv) the thermochemical reaction of metal oxides at extremely high temperature reached by solar collectors. Since the thermodynamics of CO2 at high temperature (> 1000 ºC) are quite different from those near room temperature, only chemistry below 200 ºC is discussed in this review. The one-electron reduction of CO2 to CO2 •− (eq 1) has the standard potential of −1.90 V vs. NHE,13 and is highly unfavorable owing in part to the geometric rearrangement from linear to bent.

The chemical transformation and reduction processes, electrocatalytic reduction of CO2 into valuable chemicals powered by renewable energy input is being pursued as a promising pathway to mitigate the depletion of carbon resources and environmental problems.[1] The rational design and development of electrocatalysts that are efficient, stable, and selective for this reaction is of great importance. Various metal electrocatalysts have been investigated experimentally and theoretically to rationalize their practical application in CO2 electroreduction. However, most of them commonly suffer from either low energy efficiency due to the need for high overpotentials to activate CO2 and/or low hydrocarbon selectivity due to competitive water reduction. Despite this, several advances have been made recently to substantially enhance the activity and selectivity by using nanostructured noble-metal electrocatalysts and rational modification of existing electrocatalysts. On the other hand, well-defined molecular electrocatalysts have gained tremendous attention because of their tunable reactivity and selectivity by varying the ligand structures and the coordinated metal centers. A wide variety of transition-metal complexes with nitrogen-donor ligands have been found to be active for CO2 reduction, but only few of them show impressive performances, and most of them still require quite high overpotential or give an inferior selectivity and stability.

Discussion and Conclusion:

As an abundant and non-toxic C1-building block, carbon dioxide can be reduced to various chemicals, such as carbon monoxide , methanol, formaldehyde, acetals , formic acid , formate, formamides, methylamines, formamidines, imines and methane. Recently, Beller and co-workers reported the methylation of aromatic C–H bonds using CO2 and H2 with the assistance of a ruthenium triphos catalyst. In addition to the experimental studies, there are some theoretical studies on catalytic reduction of CO2 in recent years. Pidko used a bis-N-heterocyclic carbene ruthenium CNC-pincer as catalyst and studied the mechanism of CO2 hydrogenation to formates by DFT method. Haunschildreported the catalytic reduction of carbon dioxide to methanol by using (Triphos)Ru(TMM) as catalyst. Musashi and Sakaki reported a theoretical study of cis-RuH2(PH3)4-catalyzed hydrogenation of CO2 into formic acid.