

# Involvement of Metal Complexes in Carbon Management

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**Abstract**—Increasing concentration of CO<sub>2</sub> in the atmosphere contributing potential negative impact to the environment and has been the subject of worldwide attention over the past few years. Increasing concentration of CO<sub>2</sub> in atmosphere influences the balance of incoming and outgoing energy in the atmospheric system, leading to the raise of average surface temperature of earth. Thus, CO<sub>2</sub> has often been cited as the primary anthropogenic greenhouse gas (GHG) as well as the leading culprit in climate change. Capture and sequestration of Carbon Di oxide has been considered as one of the best options to reduce CO<sub>2</sub> emission. Varieties of technologies and methods have been developed for carbon capture and utilization but none can provide a sustainable option. Proposed research highlighted the involvement of Cd, Pd, Ag, Au and Hg metal complexes for carbon di oxide capture and utilization process. The proposed complex possibly affects the carbon capture rate of biological catalyst like carbonic anhydrase. Hence a hybrid system can be proposed by involving chemical and biological catalyst for better management. The activity of Carbonic anhydrase seems to be modified theoretically by using above complexes in the light of Hard-Soft Acids and Bases (HSAB) concept. Natural zinc in the presence of some bridging ligand and heavier metal provides an extensive  $\pi$ -cloud framework for better carbon capture and utilization. Suggestive mechanistic pathway summarized as follows:

- Nucleophilic attack on carbon dioxide molecule by zinc-bounded hydroxyl group (Zn-M HO<sup>-</sup>) gives rise to the formation of the ligand-enzyme-bicarbonate ion complex;
- Release of bicarbonate ion by the displacement of a water molecule
- Intramolecular proton transfer.

**Keywords:** Carbon Capture; Metal Complexes, Carbonic anhydrase, Hybrid technique, HSAB concept

## 1. INTRODUCTION

Increasing concentrations of atmospheric carbon dioxide resulting from anthropogenic emissions is one of the greatest environmental concerns facing our civilization today. Increasing concentrations of atmospheric greenhouse gases are enhancing the natural greenhouse effects which cause a

climate change and rise in the global average temperature. Due to the huge industrialization all through the world, the concentration of CO<sub>2</sub> has gradually increased, which is responsible for the growing up of average global surface temperature of 0.6° C over the past century [1]. To mitigate the problems caused by GHGs, reduction of CO<sub>2</sub> emission especially coming from fossil fuelled industrial flue gas is a major concern to the researchers for its high impact on mankind and environment. Thus, carbon capture and sequestration (CCS) technologies that efficiently capture CO<sub>2</sub> from existing emission sources will play a vital role until more significant modifications to the energy infrastructure can be realized [2]. The capturing technology can be classified into three pathways, known as, (a) Pre-combustion capture, (b) oxy-fuel combustion capture and (c) post-combustion capture [3,6]. CO<sub>2</sub> can be captured by different techniques such as chemical absorption, physical adsorption, liquefaction or cryogenic separation, membrane based separation, and biological separation [4] [5] [6]. Among these separation techniques chemical absorption and physical adsorption techniques are the most promising for capturing post combustion CO<sub>2</sub> because CO<sub>2</sub> captured by cryogenic means is a high energy demanding process and membrane separation and biological separation are still at their nascent stage [7,6]. Since the first half of the last century removal of carbon di oxide from polluted gaseous mixtures has been successfully accomplished by absorption into both organic and aqueous liquid solvents. Absorption into aqueous solutions of alkanolamines, borrowed by the petrochemical industry, is by far the most investigated and better characterized process. This process entails an inherent energy penalty related to amine regeneration which spans between 2.7 and 3.3 GJ/tCO<sub>2</sub> [8, 9]. Extensive research has been targeted at the selection of amines characterized by good performances in terms of absorption enhancement ([10, 9] and minimize the capture costs. Among them, a sustainable approach to carbon di oxide capture has been proposed based on the use of the carbonic anhydrase enzyme and metal complexes as an absorption promoter.

Carbonic anhydrase is an ubiquitous natural biocatalyst found in all the kingdom of life that may be produced via fermentation and easily disposed of without any detrimental impact on the environment. In this regard, the most significant challenge for CO<sub>2</sub> capture at present is the large energy penalty associated with the capture. CO<sub>2</sub> capture from a post-combustion flue gas using the most highly developed current technologies involving aqueous alkanolamine solutions carries an energy penalty of roughly 30% of the output of the power plant, most of which is associated with the liberation of the captured CO<sub>2</sub> from the capture medium process [11]. Thus, minimization of the energy input for regeneration, through fine-tuning of the thermodynamics of the interaction between CO<sub>2</sub> and the adsorbent, for example, is one of the most crucial considerations in improving the energy efficiency of CO<sub>2</sub> capture [2]. Metalorganic frameworks are a new class of materials that could serve as an ideal platform for the development of next-generation CO<sub>2</sub> capture materials owing to their large capacity for the adsorption of gases and their structural and chemical tenability [12, 13, 14, 15, 2]. The ability to rationally select the frame-work components is expected to allow the affinity of the internal pore surface toward CO<sub>2</sub> to be precisely controlled, facilitating materials properties that are optimized for the specific type of CO<sub>2</sub> capture to be performed (post-combustion capture, pre-combustion capture, or oxy-fuel combustion) and potentially even for the specific power plant in which the capture system is to be installed. For this reason, significant effort has been made in recent years in improving the gas separation performance of metalorganic frameworks, and some studies evaluating the prospects of deploying these materials in real-world CO<sub>2</sub> capture systems have begun to emerge [16, 17]. Thus use of Metal-organic frameworks (MOFs) in CCS technologies will also complement other crucial strategies, such as improving energy efficiency switching to low intensive carbon fuels and phasing in the use of renewable energy resources. Keeping the above facts in view, the present study has been planned to execute the following objective:

- To study the effect of carbon capture in amines in the presence of carbonic anhydrase with or without the use of synthetic complexes of some heavier element eg. Cd, Ru, Pd, Ag, Au, and Hg etc.
- Utilization of captured carbon di oxide as a chemical resources using carboxylation reaction with biolos and poloyls.

## 2. CARBON CAPTURE AND SEQUESTRATION

A number of new concepts that may result in CO<sub>2</sub> control have been developed which include oxy-fuel combustion, pre-combustion, post-combustion process, decarbonization as well as chemical looping combustion. Among these CCS technologies, the post-combustion process is more suitable for CO<sub>2</sub> capture. At present, four technologies have been developed for the post-combustion process, e.g. solvent

absorption, adsorption using solid sorbent, membrane separation, and cryogenic fractionation.

**2.1 Pre-combustion capture:** Pre-combustion capture involves the reaction of a primary fuel with oxygen or air to produce H<sub>2</sub>. In some cases the produced gas mixture is mainly composed of CO and H<sub>2</sub>, which is known as synthesis gas (syngas). The CO formed is further reacted with steam in a catalytic reactor, called a shift converter, to give CO<sub>2</sub> and more H<sub>2</sub>. The separation of CO<sub>2</sub> and H<sub>2</sub> then can be achieved by a number of technologies.

**2.2 Post-combustion capture:** Post-combustion capture requires removing CO<sub>2</sub> from flue gas, comprised mainly of N<sub>2</sub> and CO<sub>2</sub>, before emission into the atmosphere. [18].

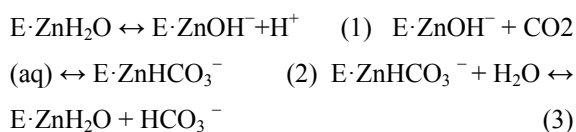
**2.3 Oxy-fuel combustion:** Oxy-fuel combustion refers to the combustion of pulverized coal or other carbon-based fuels in the presence of pure oxidizing environment and represents a relatively new process for mitigating carbon dioxide emissions compared with pre-combustion and post-combustion CO<sub>2</sub> capturing process.

In the following sections, we describe the main existing CO<sub>2</sub> capture technologies in the context of these performance considerations, namely, aqueous alkanolamine solutions and porous solids, such as zeolites and activated carbons but none of the materials fulfill all of the criteria mentioned above, which highlights the urgent need for new materials to emerge that improve upon the characteristics of these materials. In this regard, metalorganic frameworks represent an opportunity to create next-generation materials that are optimized for real-world applications in CO<sub>2</sub> capture. However, the other types of materials also carry a number of advantages, and further optimization of these materials could also potentially allow development of suitable candidates that satisfy many of the performance criteria [2].

## 3. 3. CARBONIC ANHYDRASE

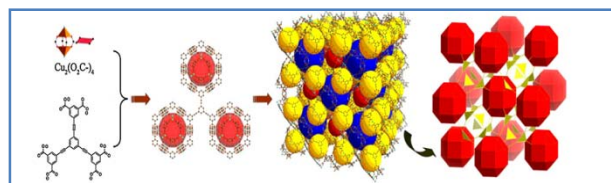
Carbonic anhydrases enzymes are zinc containing metalloproteins, which is efficiently use as a catalyst in the reversible conversion of carbon dioxide to bicarbonate and release proton. Carbonic anhydrases play important role in the CO<sub>2</sub> capture from various organs and atmosphere. Recently an emerging application of CA has begun as a carbon capture in the form of CO<sub>2</sub>. The basic hypothesis is that enzyme containing hydrophobic pockets, for which CO<sub>2</sub> acts as a substrate or product, may be used for capturing of CO<sub>2</sub> [19, 20]. Simulation studies suggested that the hydrophobic region of the active site sequesters the CO<sub>2</sub> substrate and orients the carbon atom suitably for nucleophilic attack by the zinc-bound hydroxide [21]. Techniques used for the capturing gaseous CO<sub>2</sub> are quite useful and have potential to control the climate change and green house effect [20]. Application of immobilized CA, which catalyzes the reversible hydration of

CO<sub>2</sub> to HCO<sub>3</sub><sup>-</sup> and H<sup>+</sup>, will be helpful in designing an economically feasible carbon capture system. In recent years, several laboratory scale reactors are designed to capture CO<sub>2</sub> from a gas into a liquid, based on use of CA as an approach to control greenhouse gases emitted from fixed sources [22]. Carbonic anhydrase enzymes are among the fastest known in nature with conversion rates that are typically between 10<sup>4</sup> and 10<sup>6</sup> reactions per CA molecule per second for different forms of CA [23, 24, 25]. Nucleophilic attack on the carbon atom of CO<sub>2</sub>(aq) by a zinc-bound OH<sup>-</sup> produces HCO<sub>3</sub><sup>-</sup>, which is then displaced by a water molecule. [24] suggested mechanism of carbonic anhydrase as following.



#### 4. METAL-ORGANIC FRAMEWORKS

Metal organic frameworks have recently been investigated as potential next-generation adsorbents for pressure-swing adsorption-based separation of CO<sub>2</sub> from H<sub>2</sub>. MOFs are three-dimensional nano porous extended solids composed of metal centers connected by organic molecules (called bridging ligands or linkers) [26]. Their high surface areas afford enhanced gas adsorption capacities compared with porous solids conventionally employed in multi-layer beds within current PSA systems, namely, activated carbons and zeolites, and their tunable surface chemistry is anticipated to facilitate further optimization of the material properties [2]. Metal-organic frameworks (MOFs) are made by linking inorganic and organic units by strong bonds (reticular synthesis). The organic units are ditopic or polytopic organic carboxylates (and other similar negatively charged molecules), which, when linked to metal-containing units, yield architecturally robust crystalline MOF structures with a typical porosity of greater than 50% of the MOF crystal volume. The surface area values of such MOFs typically range from 1000 to 10,000 m<sup>2</sup>/g, thus exceeding those of traditional porous materials such as zeolites and carbons [27]. In addition to zeolites and carbon-based materials, other classes of porous materials are emerging as potential adsorbents in CO<sub>2</sub> capture applications, including covalent-organic frameworks [28, 29]. Metal-organic frameworks bounded with unsaturated metal cation sites are also play potential role as separation materials for the capture of CO<sub>2</sub> from flue gas streams. Like most porous materials, CO<sub>2</sub> adsorption and uptake in MOFs are pore size/volume and surface dependent. Compared to other porous materials, such as zeolites and activated carbon, most MOFs have a higher pore volume and surface area, leading to record CO<sub>2</sub> uptakes



**Fig. 1: Construction of a designed MOF, from metal containing nodes and bridging organic ligand to supramolecular building unit and then to three-dimensional framework with pores. The last image highlights the geometry of the frame work with the ligand and polyhedral cages acting as three (yellow) and twenty four (red) connected nodes respectively. [18].**

The high surface area-to-weight ratio of MOFs is such that they have enhanced capacities for CO<sub>2</sub> capture at moderate pressures compared with zeolites. While zeolites possess higher storage capacities at pressures of less than 10 bar, it has been projected that their maximum capacities are limited to one third those of MOFs at pressures greater than 10 bar. The capacities of metal-organic frameworks up to high pressures scale with the amount of active area per unit weight: activated carbon has an active area of 400–1000 m<sup>2</sup>g<sup>-1</sup>, zeolites of up to 1500 m<sup>2</sup>g<sup>-1</sup>, and frameworks of 1500–4500 m<sup>2</sup>g<sup>-1</sup> [30].

In order to improve the CO<sub>2</sub> separation performance an alternative approach of metal organic framework-based capturing techniques is through the alternative of existing carbon capture techniques.

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