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Research Article

Reviews of Regenerative Carbon Dioxide Reactions

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ABSTRACT:
In recent years, much attention has been focused on the conversion of CO_2 to hydrocarbons, and especially vehicles fuel, and oil, which has been hydrogen reduction factor. Ziang presented an article on different fuels and technologies to convert CO_2. Gasoline and kerosene are the key products, without the need for any change can be used in combustion engines. In the simplest case carbon dioxide, according to the method can be converted partially, to co and water, by using 5% copper, and smaller amounts of nickel as a catalyst. High reaction temperature and pressure and CO_2 to H_2 ratio equals 1: 4. Efforts are under way to design catalysts that operate under lower temperatures. Co interface is useful, when accompanied with H. When the catalysts are selective towards hydrocarbon structure, they are not susceptible to long-chain products and usually larger wax components are produced that broken into smaller components later. Therefore, efforts are underway, to be used in catalysts, which are sensitive to hydrocarbons with a particular chain length, and be applicable at a lower temperature. Energy issues also continued to challenge. Sandia tests in New Mexico, America, successfully, produced gasoline from CO_2, by using a solar oven as an energy source. CO_2 insertion reaction of C-H activation reactions is an important Insertion reaction where CO as catalytic converted into a C-H sigma bond. For example, CO_2 reacts with methane using vanadyl catalyst to produce some acetic acid. The synthesis of poly-carbonates by zn (ii) and cr (ii), co (iii), AL (iii) and mn (iii) as catalyst also been proposed in the literature. C-C bond formation reactions are extremely important in organic chemistry.

Keywords: regenerative, carbon dioxide, solar energy, catalyst.

[I] NTRODUCTION

Regeneration of CO_2, with the help of electrolyte platinum group metals

Regeneration of CO_2 to fuels and chemicals substance can be done by using electro platinum group metals. Value products such as carbon monoxide, formate, methanol, methane, oxalate, and even depending on the type of catalyst and environmental conditions, heavier hydrocarbons can be produced. Three types of electro-catalysts, have been identified, levels of catalytic metal complex soluble monomers chemically modified electrodes. The last case, is a new hybrid of homogeneous solution chemistry and chemistry of solid state. Transition metal complexes as catalysts have high potential to produce high-energy fuels and chemicals. Strategy of, using Redox reactions in solution, or on the surface of chemically modified electrodes have been the modern equivalent of high temperature and pressure catalytic reactions. In an electro catalytic

cell, electricity is the energy source which is used to perform the desired reaction CO_2 + H_2O CH_3OH + O_2. In the structure of an ideal cell, regenerative products, methanol and oxidation products, oxygen, are produced in separate electrons, by using solar or nuclear energy. Energy stored in the reaction, recovery through combustion in the combustion chamber, while keeping closed the cycle, net carbon will be balance. [4]

Electro-catalysis with monomeric complex

A method for electro catalytic regeneration of the CO_2 in homogeneous solutions, is using monomeric complexes that have Redox active sites, and at least one open site, which reacts with CO_2 can be done there. The majority of homogeneous catalysts solution, contained platinum group metals, including pd (porphyrin) (Porphyrin, Tetraphenyl or Tetramethyl Porphyrin) is the 2,2'-bipyridinc and l = cl and n = 1, l = co and n = 2, Ru (trapy), pd and Rh. electro catalytic regeneration of the CO_2 with complex, converted to carbon monoxide, with low potential of low and medium temperature. [4]

Electro-catalytic with thin layer of polymeric

In comparison with homogeneous systems, fixed electrode catalysts have the advantages are as follows:

1) With the increase in catalyst concentration, current density increases.

2) Use only small amounts of expensive chemicals

3) Reduce or prevent the loss of activity of the catalyst

4) The ability to obtain chemical selectivity

5) The ability to change mechanisms, by preventing or facilitating the choice of bio-molecular interactions between Redox-active polymer sites

6) Take advantage of the structures and systems of two or more layers, in order to perform spatial separation of different catalysts Activity

Here electro-catalytic properties and synthesis of thin polymeric layers containing particles entered into inner regions of Redox-active polymers chemically modified electrodes by using strategy, pursued. There are two strategies in the electro-catalytic film forming polymer: [4]

1) Regenerative electro-polymerization of vinyl (Vinyl) that contains metal complex with an unstable metal, for example,

2) The reductive electoro polymerization of precursors with ligating sites followed by blinding mutilations in the film and in situ reduction.

Performance of platinum group metals in CO_2 electro-catalyze

Platinum group metals, have an important role in CO_2 electro-catalytic regeneration and this is continued. Here focused on two methods.

1) The use of homogeneous electro-catalyst solution.

2) Polymeric layers using on the electrode surface (chemically modified electrodes) that are contained electro-catalytic sites. These sites are usually metal particles.

Previous approaches, a clear understanding of process and mechanisms of CO_2 regeneration, is started and emerged. However, after that, possibility of producing more electrons, practically the two electrons are left behind. Challenges of the future, will be to find and describe the chemically modified electrodes, for oxalate and formate, understanding the mechanisms of chemically modified electrodes in the environment. Also describes the role of the complexes of carbon dioxide, chemically modified electrodes in the electro-catalytic process, and also electro-catalyzed homogeneous, and eventually discover a new method for forming the identified organic compounds electro-catalytic, will be part of the challenge. [4]

CO_2 regeneration, by Molybdenum Catalyst

Today the focus is on strengthening the catalytic properties of p-type electrode, which light corrosion problem is not very important in the recovery process. Over voltage in produce hydrogen from the p-type electrode is usually high. However, it was found that the catalytic properties of the optical cathode si improved to

create hydrogen, when a derivative of viologen placed chemically on the electrode surface, and the particles pt are dispersed within the matrix polymer. Viologen in optical electron transfer to + H, plays a relevant role. There is a thin layer of platinum on the p-type silicon electrode and improved catalyst performance.

Charge conduction is generally much higher in electrically conductive polymer than in typical electroactive polymers.

Therefore, work on conductive charge polymer, in the field of photo-electrochemical, has been pushed to towards the stability of the electrodes against photo degradation in electric production cells. Conductive charge polymer, known as a protector of the semiconductor surface, against optical damage (photodecomposition). In one study found that, which coating the n-type silicon semiconductor optical electrodes, with the conductive charge polymer, such as poly pyrrol, leading to greater stability against oxidation of the surface of the electric production cells. Regeneration of carbon dioxide to methanol is defined as follows:

$$CO_2+6H^++6e^- \rightleftharpoons CH_3OH+H2O$$

In a study conducted by jr. frese, the reaction is carried out on the surface of the cathode of molybdenum. Accordingly, the cathode of molybdenum, can convert carbon dioxide to methane, with 80-100 percent of selectivity. In another study, Barton, Solar regeneration of CO_2 to methanol is done by using photo electrochemical cell (PEC) based on catalyzed p-Gap in a process that known as Chemical Carbon Mitigation. In another study xu, through a biochemical process which used Di Hydronaz formate enzymes, formaldehyde and alcohol as a catalyst, successfully regenerate CO2 to methane. The final catalysts even after 60 days that they were stored, have shown Methanol Yield about 76.2%. [5] The above data indicate that regeneration of CO2 to methanol and other chemicals through the use of photo electrochemical cells is better than other methods. To achieve a more efficient photo electrochemical cell for the reaction, following system must be provided:

1. The n-type semiconductor with desirable band eges and bade gap for photo anode (eg: net Tin_2, zno and cds ...)
2. N-type semiconductor with appropriate band eges and bade gap (such as: doped Tio_2, zno and Gap ...)
3. A catalyst for CO_2 regeneration reaction on or near the surface of the photo anode (such as pyridinium ions on the surface of p-Gap)

Electrochemical regeneration of carbon dioxide

As highlighted some shortcomings in the process of water oxidation, while the other half of reaction is regeneration of carbon dioxide, the overall process will be more difficult. Regeneration of carbon dioxide in comparison with the corresponding competitive reactions such as Hydrogen evolution reaction is much more complicated. Although regeneration of CO_2 in comparison with HER thermodynamically is favorable reaction, but as one of the difficulties and complexities, requires a large over voltage to perform the reaction at an appropriate rate. In addition, a wide range of products, and a plurality of different interfaces, makes it difficult to analyze from the point of view of efficient catalysts and the selectivity. Transition metal catalysts for the production of products resulting from the regeneration of CO_2, such as carbon monoxide, formate, methane, ethylene, ethanol presented. However, most transition metal catalysts are desired to produce H_2, and only a few catalysts such as cu, Au and Ag and Sn have shown good activity for the regeneration of CO_2, because the regeneration of CO_2 can lead to different products. Each catalyst shows different selectivity. Among them, Au and Ag have been considered as catalysts convert CO_2 to Co with high selectivity. Where sn has high efficiency in the production of formate. Hydrogenation of CO_2 with renewable H_2, can produce methanol or long chain hydrocarbons, which can be used as fuel or chemicals. Hydrogenation of CO_2 extensively to

identify active sites catalyst, and strengthen convert CO_2 into useful products has been studied. Best known catalysts are, composites, metal oxide - metal. Cobalt metal catalyst, based on various base to form hydrocarbons have been studied. Specifically, for the production of methanol, cu on Zno and ceo_2 been identified as active catalysts. Systematic design of catalysts, can be employed a road map for efficient catalytic conversion or intermediate products formed through multi-step reactions. Olefins, which are produced by hydrogen, commonly Hydro formulations to aldehydes, However Hydro formulations conventional process, is dangerous reaction in terms of technology, for high pressure and difficult requirements for purification. Two stack catalytic process development (Tandem) by using nanostructures, proved that the selective formation of propane, from methane and ethylene will be useful in sequencing reactions. [8]

Important factors for optic regeneration of CO_2

Comparing the activity of different telephoto catalysts reported by various groups is difficult, with only consider converting speed, or quantum efficiency, according to the difference between the method of preparation and conditions of a particular test. However, it is commonly accepted that several aspects can be considered to improve the efficiency of photocatalytic semiconductors. Photocatalyst particle size has a great effect on the regenerative capacity of optical CO_2. Reducing the particle size can sometimes lead to increase photocatalyst surface area, which provides more active opportunities to absorb CO_2. Photocatalyst with smaller particle size also benefited from a shorter transmission path for charge carriers to reach their surface. However, whatever smaller the particle, either increases particles common border. Yi et al. made $NaNbO_3$ by hydrothermal method and complex polymerization method. $NaNbO_3$ nanoparticles that made by complexes polymerization have higher surface area than the hydrothermal products. Respectively were $38m^2g^{-1}$ and 1.7 m^2g^{-1}. As a result of advances in 3-fold and 6-fold in O_2 and H_2 production rate was achieved. Several types of nanomaterials with specific morphology have a significant effect on CO_2 regenerative capacity. Such as one-dimensional nanorods and nanotubes of specific electron transport pathways, mesoporous nanostructures with high substantially surface area. Loading photocatalyst on the surface, is another common agenda to achieve additional increases on both of conversion capacity and selectivity. Commonly known that the optical regeneration reaction can be improved by loading noble metal nanoparticles. On the other hand, it is known that metal oxide nanoparticles, facilitate the oxidation reaction. Cocatalyst (catalyst plus, additional) is an important type. Some noble metals, particularly with respect to water reclamation are active, while others are better suited for the regeneration of CO_2. This is because cocatalyst, which catalytic active sites provides different absorbed species for resuscitation. The cocatalyst extract (separate) synthesized optical electrons or holes (cation) to increase the lifetime of the charge carriers. Metal oxide also does not supply catalytic regeneration reaction, and by entrusting it to the photocatalyst may increase, regeneration product yield. As it can remove holes, and increase the lifetime of electrons for regeneration reaction (ie, regeneration of CO_2 on Cu-RuOx). In addition, accompanying electrons on the cocatalyst, provides the possibility of unloading more than one electron in an instant, and multi-electron reduction process of CO_2 became easy. Type of cocatalyst in different photocatalyst, to achieve the best optical activity changes. Today, the cocatalyst functional strategy for the regeneration of CO_2, primarily focused on cocatalyst regeneration of CO_2. However, there are other strategies in photocatalytic water splitting systems or photo-electro catalytic (PEC). For example: 1. Cocatalyst oxidation to remove holes from photo catalysts 2. Binary catalyst systems for both oxidation and regeneration reactions. Noble metals Pt, Cu and Ag are three of the most common cocatalyst for optical

regeneration of CO_2. Loading (put) Pt cocatalyst is usually beneficial for the production of methane. While CO, in the presence of Cu and Ag is most preferable.

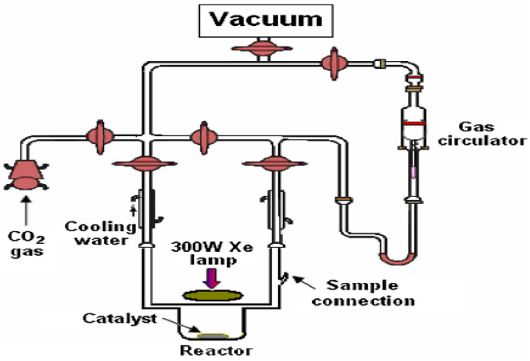

Figure 1 fluidized bed batch reaction steps for optical regeneration of CO_2

Yamakata and colleagues reported that the recombination of electrons and holes when Pt is located on the photocatalyst, strongly discouraged. Loaded Pt on TiO_2 and Zn_2GeO_4 for regeneration of CO_2 is used, and it was found that CH_4 is the only product of regeneration. However, Pt is a popular cocatalyst for water regeneration. In one of the experiments of Pt loaded on $KTaO_3$ for optical regeneration of CO_2 under UV light were used. It was found that the hydrogen yields greatly increased and is natural and untouched in compare with $KTaO_3$. While only partial CH_4 is produced. So how controlling the competitive reaction of water, is important, because the Pt may facilitate water activation (speed up). To overcome the problem, Zhai and colleagues used a binary cocatalyst Pt / Cu_2O with a porous structure / cover for regeneration of CO_2 on TiO_2. H_2, CO, CH_4 and O_2 were formed and the presence of protective layer Cu_2O will lead to higher yields of CO. Pt cocatalyst reduce CO_2 regeneration selectivity. While loading Cu_2O layer selectivity increases from 60 to 80%. It was suggested that Cu_2O layer provides preferred reaction sites to convert CO_2. While Pt cavity acts as an electron sink (deposition) for collecting optical electrons generated by TiO_2. So put layer of Cu_2O on Pt, particularly increased regeneration of water to H_2; competitive reaction with the revival of CO_2. Copper and silver in large quantities as cocatalyst for regeneration of CO_2 are used. Cu having the effect of electron capture to prevent recombination of electron-hole; loading Cu over $BaLa_4Ti_4O_{15}$, ZrO_2, SiC and TiO_2 can improve their effectively optical activity. Peterson and colleagues studied the mechanism of Cu as cocatalyst for the regeneration of CO_2. They found the weak link of CO to copper surface, prevent the formation of adsorbed CO to CHO, which is an important intermediate for hydrocarbons. Loaded Ag on BaLa4Ti4O15, $SrTiO_3$ and TiO_2 have been used for optical regeneration of CO_2. It is necessary to point out that the addition of Ag, Cu and NiOx to $BaLa4Ti_4O_{15}$ as cocatalyst resulted in optical regeneration of CO_2. While H_2 and O_2 only for natural and unspoiled $BaLa4Ti_4O_{15}$ was discovered. When Ru and Au have also been loaded, the increase in products H_2 and O_2 were observed but no CO found. This results showed that both Cu and Ag can be used as reaction sites for the regeneration of CO_2 and electron capture function. Although cocatalysts for improving the photocatalytic activity of noble metals are known, inexpensive cocatalysts progress seems to be much more important. By updating, several types of non-noble metal catalysts such as NiO, Co-Pi, MoS_2 and WS_2 are used in photocatalytic reactions. Kudo and colleagues in the general separation of water by Ni / NiOx loaded, La doped on $NaTaO_3$, reported in the year 2000. Then NiO as catalyst on $InTaO_3$, $Sr_2Nb_2O_7$ and Sr_2Ta_2O etc. was used. Co-Pi at first for accelerating the oxidation of water was reported in 2008 that could drastically reduce the Overvoltage required for water oxidation. Durant and colleagues recently studied the dynamics of charge carriers by light in the Co-Pi, loaded on Fe_2O_3 by passing absorption spectroscopy. Upgrade to increase the life of optical cavity made, were attributed at least three times big. Recently, Wang and colleagues added MgO on TiO_2, to promote chemical adsorption of CO_2 on the catalyst surface is reported, which greatly speeds up the regeneration of the

photocatalytic CO_2 to CH_4. Tungsten and molybdenum sulfide and also for the regeneration of the CdS; the non-noble metal as cocatalyst may act for the regeneration of CO_2, it has been reported. Increase water separation on $NaTaO_3$ coupled with $[MO_3S_4]^{3+}$ is also specified. However, the journal of stability and safety of metal sulfide compounds, may limit their practical usability. As a result, several factors are important for a good photocatalyst such as small particle size, high surface area, the figure directly has been exposed, along with long-lasting charge carriers. In addition, although the photocatalyst is suitable for the regeneration of CO_2 optical synthesized electrons and holes may recombined; if no site active / available appropriate reaction on the surface of an optical detector semiconductor is not present. So adding catalytic active sites for the recovery of CO_2, on the surface of the semiconductor by loading cocatalyst is necessary. [16]

CONCLUSION

Separate and remove carbon dioxide from the atmosphere is a concern for the last few decades' scientists. To do this many ways. One of the new methods for trapping carbon dioxide from gas mixtures generated by the combustion of fossil fuels, is the use of hydrate crystals. Basis of separation or trapping carbon dioxide, is the fact that the volume of carbon dioxide into hydrate crystals is different with its volume in the gas mixture after combustion. In the present study the separation of carbon dioxide from the combustion gas mixture by using hydrate formation is checked. According to the results, this method in comparison with other methods, high purity carbon dioxide is separated. In ammonia and urea fertilizer producing companies, which their consumption feed is natural gas with high methane content, or so-called light gas, usually the ratio of ammonia to carbon dioxide is more than required ratio in the urea unit, and therefore, this companies are faced with excess ammonia. Since Khorasan Petrochemical Complex, also not exempt from this rule, and is faced with an increase in liquid ammonia, so this company in order to solve this problem, and in order to increase the capacity of urea plant, need to have another source to compensate carbon dioxide, to provide urea plant feed, with excess ammonia, And since the combustion gases in the stack of ammonia unit reformer furnace is containing 12% carbon dioxide, separating carbon dioxide from exhaust gas reformer furnace, is taken into consideration. On the one hand due to the harmful effect of greenhouse gases, the most important of which is climate change, it is necessary to adopt measures to prevent the uncontrolled spread into the atmosphere. In recent decades, various mathematical models described on membrane performance but in terms of simulating separation processes, by using membrane models with available simulators, less work has been done.

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