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Mini Review

Photo-catalytic Conversion of CO_2 to Hydrocarbons: Introduction, Challenges and Possible Approaches

Xiangchao Meng and Zisheng Zhang*

Department of Chemical and Biological Engineering, University of Ottawa, Canada

***Corresponding author :** Zisheng Zhang, Department of Chemical and Biological Engineering, University of Ottawa, Ottawa, K1N6N5, Canada.

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Abstract

Photo-catalytic reduction of CO2 to produce valuable hydrocarbons is a promising process to not only alleviate the issue of massive CO2 emissions, but also provide a strategy to convert solar energy to chemical energy. It has been extensively studied in last 10 years. In this brief review, the basic concepts as well as an introduction of this advanced process are included. Meanwhile, challenges and possible approaches are also pointed out. Future works were also suggested at last.

Keywords: Photocatalysis; CO_2; CO_2 reduction; Solar energy

Introduction of Photo-catalysis and its mechanism in Co_2 reduction

Photo-catalysis has extensively studied since the first report in 1972 [1]. This technique theoretically aims to convert light energy into chemical energy. As for the mechanism, it can be interpreted as electrons on the conduction band (CB) of a semiconductor may be activated and jumped to its valence band (VB) with positive holes left behind. The separated charge carriers (electrons and holes) may be recombined, or transfer to the bulk surface to react with adsorbed water/oxygen to produce oxidative free radicals (such as •OH, •O_2- etc.), or other adsorbed species (such as organics, CO_2, NO, bacteria, etc.) [2-8].

From the aspect of types of reactions, the applications of photo-catalysis can be simply divided into two categories, namely, advanced oxidation processes (AOPs) and photo-reduction processes. As for the AOPs, the effective species are photo-generated holes and generated oxidative free radicals, these processes are widely applied in decomposition of pollutants in waste water and polluted air, and bacteria inactivation or disinfection. And for the reduction processes, it mainly includes water splitting to evolve H_2, heavy metal ions recovery, CO_2 reduction and N2 fixation. As a promising approach to convert CO_2 to valuable hydrocarbons, photo-catalytic reduction of CO_2 has been immensely studied in last 10 years. As shown in Figure 1, it summarized the number of documents about photo-catalytic reduction/ conversion of CO_2 by year, the number of related documents in the year of 2017 is about 7 times higher than that in the year of 2010. It suggests this research area is a promising and rapidly being developed topic in recent years and will possibly last long.

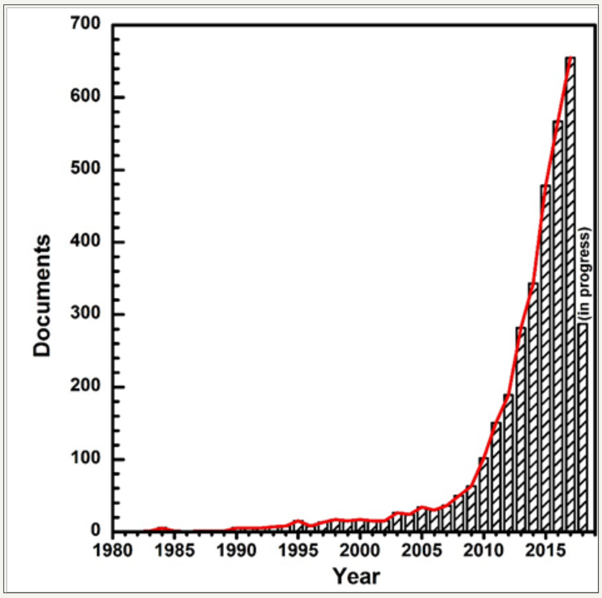

Figure 1: Documents by year with search the keywords 'CO_2 reduction photocatalysis' or 'CO_2 conversion photocatalysis' on April 18, 2017 using Scopus

In Inoue et al. [9] for the first time, reported on photo-catalytic reduction of CO_2 to produce hydrocarbons. The photo-catalytic reactions occurred in CO_2 reduction can be considered to the follow schemes. The separated electrons and holes (reaction 1) can separately react with dissolved CO_2 and adsorbed water (reaction 2). It is more complicated for the reductions, formic acid, formaldehyde and methyl alcohol may be produced (Reaction 3-6). The feasibility of CO_2 reduction for a semiconductor is significantly determined by the conduction band potential. As shown in Figure 2 [10], only electrons on the conduction band with higher reduction ability are capable of convert CO_2 to hydrocarbons. The formation of products is different, which depends on the number of electrons and protons taking part in the chemical reactions. For example, to form CH4 from CO_2, eight electrons and eight protons are required (Reaction 3-6). The selectivity of products is a significant problem for photo-catalytic reduction of CO_2, which is affected by many factors, such as reaction conditions, red-ox potentials and the type of substrates. From the point of thermo dynamic, CO_2 is too stable to be reacted. The structure of CO_2 (O=C=O) consists of a linear connection between carbon and two oxygen atoms. The Gibbs free energy for the CH_4 and CH3OH is -51 and -166kJ/mol, which is higher than that for water splitting. This determines CO_2 reduction is an incredible endothermic process, and more complicated compared to the water splitting process [11,12].

$$\text{catalyst} + h\nu \rightarrow \text{catalyst}\,(e^-_{CB} + h^+_{VB}) \qquad (1)$$

$$H_2O + h^+_{VB} \rightarrow \frac{1}{2}O_2 + 2H^+ \qquad (2)$$

$$CO_2(aq) + 2H^+ + 2e^-_{CB} \rightarrow HCOOH \qquad (3)$$

$$HCOOH + 2H^+ + 2e^-_{CB} \rightarrow HCHO + H_2O \qquad (4)$$

$$HCHO + 2H^+ + 2e^-_{CB} \rightarrow CH_3OH \qquad (5)$$

$$CH_3OH + 2H^+ + 2e^-_{CB} \rightarrow CH_4 + H_2O \qquad (6)$$

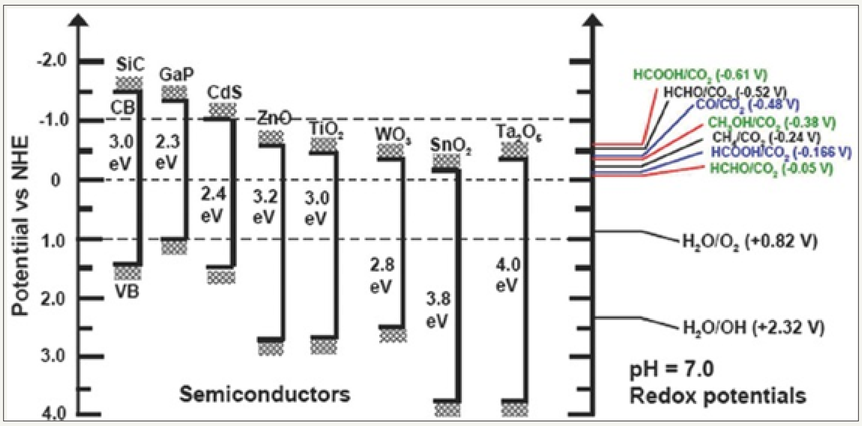

Figure 2: Band structures of various semiconductors relative to the redox potentials at pH 7 of compounds involved in CO_2 reduction (Adapted from [10], © 2014 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim).

Challenges and Possible Approaches

Photocatalytic activity

One of the ideal energy sources for photo-catalysis is solar light. The solar-driven photo-catalytic reduction of CO_2 to hydrocarbons is also called artificial photosynthesis. One of the primary hindrances for this process is its low activity under visible light, as for TiO_2 is a typical and commercialized photo-catalyst, only responsive to ultraviolet (UV). Approaches to overcome this shortage were adopted, and can be divided into two categories, namely, modification of TiO_2 [13-15] and preparation of visible light-responsive photo-catalysts [16-19]. Since CO_2 is a stable molecule, the photo-catalytic activity of a bare semiconductor is poor, and various modifications are generally required to improve the photo-catalytic activity in the CO_2 reduction. As for the effective approaches, they are comprehensively reviewed in [20]

Selectivity

As electrons on the conduction band are capable of react with various adsorbed species and the various hydrocarbons may be formed. It is significant to improve the selectivity of specific products. Meanwhile, hydrogen may also be generated, which will decrease of selectivity of hydrocarbon products. Dong et al. [21] have reported on improve the selectivity of CH4 in photo-catalytic reduction of CO_2 via adjusting the size of platinum nanoparticles (Figure 3). Kumar et al. [22] have reported on photo-catalytic reduction of CO_2 to selectively produce methanol without addition of sacrificial agents on graphene oxide supported heteroleptic ruthenium complex.

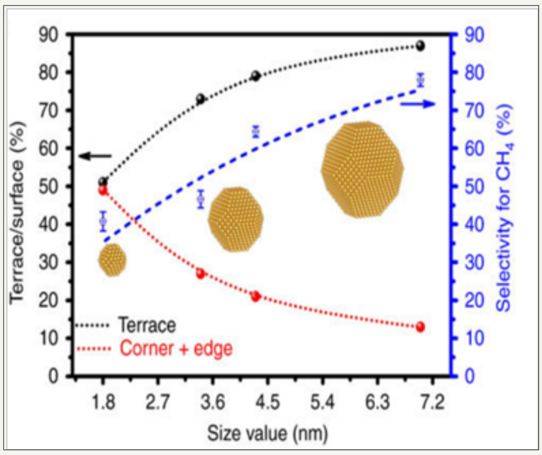

Figure 3: Correlations between the selectivity for CH4 and surface site proportion as functions of the size of Pt NPs (Adapted from [21], Copyright © 2018, Springer Nature).

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Experimental Conditions

Various experimental conditions influenced the photo-catalytic reduction of CO_2. For example, Mizuno et al. [23] reported on the influence of CO_2 pressure on the photo-catalytic reduction CO_2. They found that with increase the pressure of CO_2, it will accelerate the CO_2 reduction process. Another critical issue for photo-catalytic reduction is the carbon source, carbonaceous residues on the photo-catalysts surface which may be from the synthesis process and the laboratory atmosphere, significantly influence the CO_2 reduction and possibly contribute to the overall product yield.

Conclusion and Outlook

Photo-catalytic reduction of CO_2 to produce valuable hydrocarbons is a promising process. However, as for the low conversion efficiency, low selectivity of a specific product, and unsatisfactory light harvesting, more and more efforts should be done before it's widely applied in practice. Also, mechanisms for this complex processes should be clearly clarified in future works. The key to boost the feasibility of this process is to develop advanced materials with high visible light-responsive activity and high selectivity, such as recently developed plasmonic photo-catalyst. Try to combine with other advanced techniques such as electro catalysis would be another approach to enhance the development of this process. To use it in industrial scale, photo reactor design would be another issue to be conducted.

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