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FUNDAMENTAL STUDY OF THE PHOTOCATALYTIC REDUCTION OF CO_2: A SHORT REVIEW OF THERMODYNAMICS, KINETICS AND MECHANISMS

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On the off chance that methods which reduce the global CO_2 content are unavailable and inefficient, the increasing CO_2 levels will lead to a synchronized rise in temperature across the world. The conversion of this abundant CO_2 into hydrocarbons like CH_4, CH_3OH, CO, HCOOH and hydrogen fuel using different techniques and their use for power could assist with the world's energy deficiency and solve the CO_2 reduction-energy nexus. In this study, photocatalytic CO_2 conversion by sunlight will be of primary focus since this bears a resemblance with the regular photosynthesis phenomenon. This work also portrays the writings that have narrated the development of mixtures of two or more carbon ions (C^{2+}) within the photocatalytic reduction of CO_2. This paper thus comprises the energy required for CO_2 photoreduction, the kinetics mechanisms and thermodynamics requirements. The reaction of CO with water and the hydrogenation of CO_2 are covered to understand the gap of Gibb's free energy between both of the reactions. Likewise, the summary of different metal-based co-catalysts, metal-free co-catalysts and their selectivity towards CO_2 reduction by photocatalysis and reduction of CO_2 into various hydrocarbons, fuel and materials have also been examined.

Keywords: CO_2 to fuels, hydrocarbon production, thermodynamics, photocatalysis, mechanism

1. INTRODUCTION

The ever-growing industrialization and increasing dependence on a carbon-based society have resulted in very high CO_2 emission levels. This rise in CO_2 has become a genuine natural issue and it has detrimentally contributed to climate change. Conversion of CO_2 using sunlight and water into chemical compounds using photocatalysts, emulating a regular photosynthetic technique, is one of the best and the most encouraging methodologies for diminishing air CO_2 emissions, an activity that would add to climate change relief while giving inexhaustible energy. Photocatalytic reduction of CO_2 has been studied extensively in this regard. The survey is more prominently centered around investigations on photocatalytic CO_2 reduction,

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specifically the materials with more than one carbon, conventionally named as C^{2+} items (Albero et al., 2020). Besides this, the photocatalytic CO_2 with H_2O via different titanium oxide nanoparticles, titanium-free metal-based catalysts have additionally been looked at. This paper also addresses some bottlenecks of CO_2 photoreduction that have not been studied extensively, for example, the reaction mechanisms and pathways of photocatalysis involving multiple electron transfers are very difficult to explain because of the high energy proton-barriers, complicated activation and adsorption of CO_2 molecules, formation of unwanted side products, lower efficiency, and the complicated absorption of different types of molecules on the surface of semiconductors.

2. THERMODYNAMICS, KINETICS AND MECHANISMS OF PHOTOCATALYTIC CO_2 REDUCTION

2.1. Thermodynamics of photocatalytic CO_2 reduction

The thermodynamics of CO_2 reduction reactions depend on the redox potential and Gibbs free energy. For multi-electron reactions, the Gibbs free energy should be positive for the reaction to be spontaneous. The hydrogenation of CO_2 can be achieved by the thermal reduction of CO_2 with the help of high-energy H_2. The use of H_2 as a reducing agent aids the production of CH_3OH and inhibits the formation of methane over Cu-loaded In_2O_3/TiO_2 photocatalysts (Tahir et al., 2016). As shown in Fig. 1, the electrons are responsible for the reduction of CO_2 to low carbon fuels and the holes react with water to produce O_2. In theory, for CO_2 photoreduction to occur, the conduction band level of the semiconductor should be higher than the reduction potentials of CO_2, whereas, the valence band level should be more positive than the oxidation potentials. Table 1 shows some electrochemical reactions with standard potential ΔE^0 at pH 0 and 25 °C. This given data is illustrated in graphical form as shown in Fig 2. Table 1 shows that the

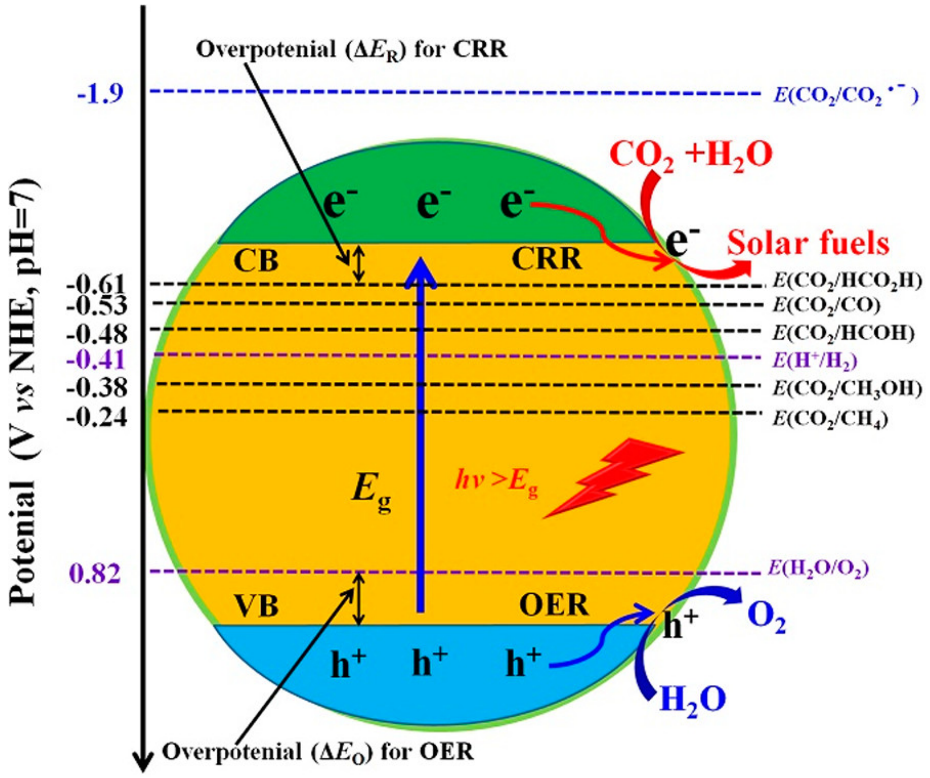

Fig. 1. Representation of CO_2 photoreduction in a semiconductor. Reprinted from (Li et al., 2019) with permission of ACS Publications

one-electron reaction for the formation of $CO_2^{\bullet-}$ radical required a very costly and very high voltage. Hence, thermodynamically we can conclude that reactions with a higher number of electrons for the formation of CO_2 to other products are preferable because of lower thermodynamic consequences.

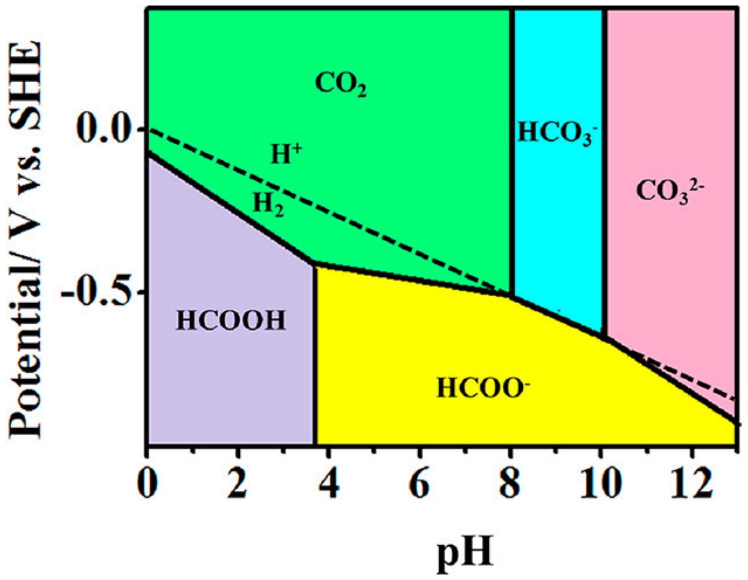

Fig. 2. Graphical representation of the formation of various products as a function of pH at 25 °C. Reprinted from (Li et al., 2019) with permission of ACS Publications

Table 1. Standard potentials for CO_2 reduction reactions (Lehn and Ziessel, 1982; Morris et al., 2009; Vayenas et al., 2008; Willner et al., 1987; Yahaya et al., 2004)

Electrochemical half-reactions	Standard potential ΔE^0
$2H^+ + 2e^- \rightarrow H_2(g)$	0
$2H_2O(l) + 4h^+ \rightarrow O_2(g) + 4H^+$	1.229
$CO_2(g) + e^- \rightarrow CO_2^-$	–1.9
$2CO_2(g) + 2H^+ + 2e^- \rightarrow H_2C_2O_4(aq)$	–0.475
$CO_2(g) + 2H^+ + 2e^- \rightarrow HCO_2H(l)$	–0.2
$CO_2(g) + 2H^+ + 2e^- \rightarrow CO(g) + H_2O(l)$	–0.12
$CO_2(g) + 4H^+ + 4e^- \rightarrow C(s) + 2H_2O(l)$	0.21
$CO_2(g) + 4H + +4e^- \rightarrow HCHO(l) + H_2O(l)$	0.07
$CO_2(g) + 6H^+ + 6e^- \rightarrow CH_3OH(l) + H_2O(l)$	0.03
$CO_2(g) + 8H^+ + 8e^- \rightarrow CH_4(g) + 2H_2O(l)$	0.17
$2CO_2(g) + 8H_2O(l) + 12e^- \rightarrow C_2H_4(g) + 12OH$	0.07
$2CO_2(g) + 9H_2O(l) + 12e^- \rightarrow C_2H_5OH(l) + 12OH^-$	0.08
$3CO_2(g) + 13H_2O(l) + 18e^- \rightarrow C_3H_7OH(l) + 18OH^-$	0.09

2.2. Kinetic study of CO_2 photoreduction and reaction mechanism

The kinetics of CO_2 photoreduction is explained by the Langmuir–Hinshelwood-based model. The upside of utilizing this methodology is that it remembers the effect of partial pressure and irradiance on the kinetic information as shown in Eq. (1). The weakness of this model is that it is very time-consuming and human efforts are needed to gather CO_2 photoreduction kinetic information. According to this model, the rate of reaction is defined as a measure of photoactivity of catalyst, which can be written in terms of the number of moles divided by multiplication of unit time and reaction space. This review also covers the factors like effect of irradiation, temperature and pressure on kinetics. During the photocatalysis process, distribution of UV-light and absorption of this light by photocatalyst are the two major factors in the development of kinetic models. Equation (1) clearly shows that the rate of reaction is directly related to irradiation.

$$r = kI^{\alpha}\frac{\prod_{i=1}^{n} KiPi}{\left(1+\sum_{i=1}^{z} KiPi\right)^{n}} \tag{1}$$

where r is the rate of the reaction (μmol gcat^{-1} h^{-1}), k is the rate constant (μmol gcat^{-1} h^{-1}), I is the irradiance; α is the reaction order of light intensity (dimensionless); Ki represents the equilibrium adsorption constants for reactants and products (bar^{-1}); Pi refers to the partial pressures for reactants and products (bar); n indicates the adsorbed reactants that are involved in the elementary surface reaction and z indicates all reactants and products. On the other side dependency of temperature is not shown in Eq. (1) but an increase in temperature also increases the diffusion of molecules, expanding the likelihood of reagent crashes on the photocatalyst surface and increasing the collision rate of molecules on the surface of the catalyst hence increasing the rate of reaction. Also, selectivity towards different products depends on temperature. As shown in Eq. (1) partial pressure of CO_2 and reagents directly affect the rate of reaction. Also, the inlet pressure of the gas during photocatalytic reaction plays a crucial role in it. Adsorption and activation of CO_2 play an important role in increasing the photocatalytic activity for the reduction of CO_2 by photocatalysis. To define the rate-limiting step, we consider the formation of adsorbed CO_2 on the surface of the semiconductor. This step explains how energy may reorganize itself between an ion radical $CO_2^{\bullet -}$ and the linear CO_2 molecule, which is ruled by electronic band structures, crystal phases and surface properties. To achieve high CO_2 adsorption, the increment of the active sites is of paramount importance. For that to occur, the fabrication of mesoporous metal semiconductors is the preferred technique. This technique enhances CO_2 adsorption and activation by creating increased surface area, making the distribution of pores uniform. Thus, by using mesoporous semiconductors we can efficiently promote charge transfer and increase the rate of photoreduction. From the literature quoted thus far, we can conclude that CO_2 can be converted into multiple compounds such as CO, HCOOH, CH_3OH and CH_4.

Multiple photocatalysts have been studied and employed for the reduction of CO_2 by using H_2 or H_2O to form different products. Before choosing an appropriate photocatalyst for reduction, the reaction mechanism needs to be specified first. This reaction mechanism can be classified as (i) mechanism derived from *OCHO, (ii) mechanism derived from *COOH (Lingampalli et al., 2017). In the first one CO_2 is attached to the surface of catalysts through O_2 by acceptation and donation of electron/proton and forms the defined intermediate. The second mechanism follows the same way but here CO_2 is attaching to the surface of catalysts through carbon. Similarly, by acceptation and donation of two-electron pair or multiple electron/proton pair and by following different pathways we can convert CO_2 into different products as shown in Fig. 3. So for any particular product, we can easily describe the production pathway using these reaction mechanisms.

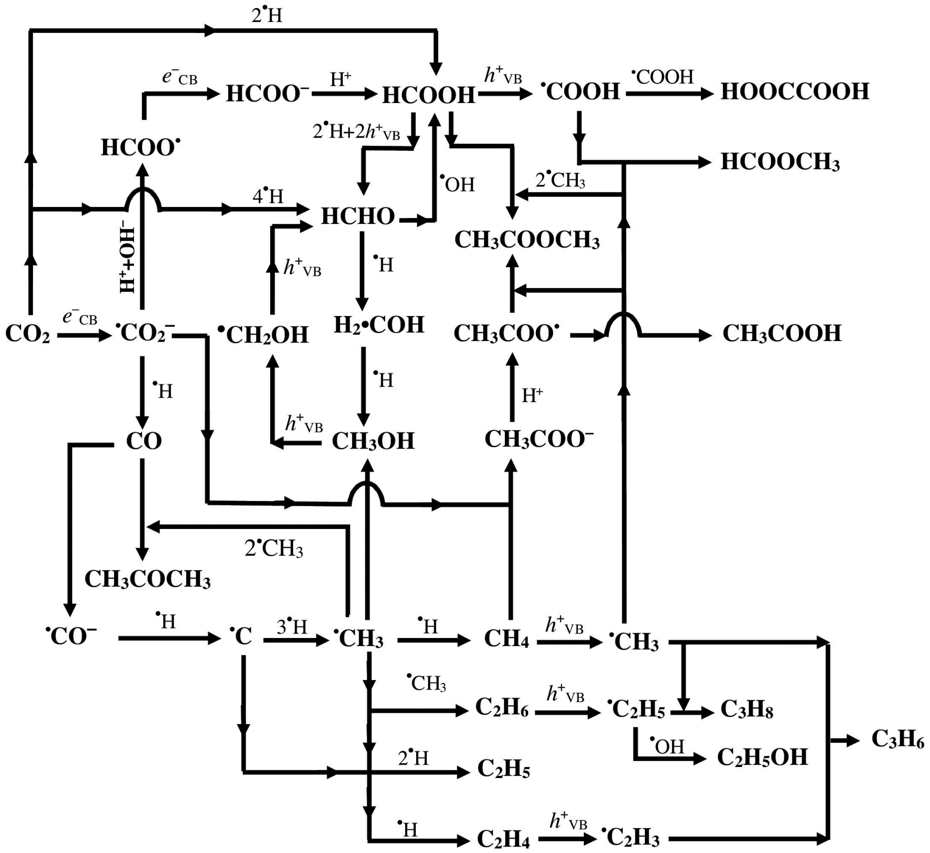

Fig. 3. Representation of mechanisms for reducing CO_2 with the use of different catalysts, with a couple of possible pathways. Reprinted from (Karamian and Sharifnia, 2016) with permission of Elsevier Ltd.

3. CONCLUSIONS

This review covered the conversion of CO_2 into useful products with the help of semiconductors and different types of photocatalysts. By the use of appropriate reaction mechanisms, pathways and also by using suitable cocatalysts, it is easy to predict the selectivity of CO_2 photocatalytic reduction. Kinetics helps to understand the geometry of the light source. Also, the effect of temperature, pressure and light transport on the rate of reaction is discussed. From thermodynamics, it is clear that the positive value of Gibbs free energy (ΔG^0) and the reaction which contains more than one electron is beneficial. As per the thermodynamics, hydrogenation of CO_2 is favorable. Also, the use of water in photocatalytic reactions will fulfill the need for hydrogen requirement during the reaction. Fabricated semiconductors increase the adsorption of CO_2 and enhance activation hence giving a better understanding of reaction kinetics. Making of composites by the use of these semiconductors and use of these composites in photocatalytic reduction of CO_2 is in high development.

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