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Reduction of CO_2 photocatalyzed by Cu-TiO_2-based catalysts: a review

Reducción de CO_2 foto catalizada por catalizadores basados en Cu-TiO_2: una revisión

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Abstract

The continuous combustion of non-renewable fossil fuels and the depletion of the natural resources from which they come and, consequently, the continuous increase of carbon dioxide (CO_2) emissions into the atmosphere are intensifying the search for the conversion of carbon dioxide to fuels and value-added chemicals, with the main objective of reducing emissions and creating renewable and sustainable energy sources. In this sense, there is a lot of interest in the photocatalytic reduction of CO_2 with H_2O, mainly using solar energy, which is a renewable source with a continuous and easily available light supply. Recent progress in this area has focused on the development of promising photocatalysts, primarily based on TiO_2. In this context, this article analyzes: (i) the role of CO_2 in the treatment of problems related to energy and global warming, (ii) the fundamental knowledge of the photocatalytic reduction of CO_2, (iii) the role of the catalysts of copper-doped TiO_2 in the photocatalytic transformation CO_2; as well as (iv) emerging and crucial opportunities for future research employing Cu-TiO_2 photocatalysts; mentioning the most up-to-date relevant references.

CO_2, photocatalytic reduction, Cu-TiO_2

Resumen

La combustión continua de combustibles fósiles no renovables y el agotamiento de los recursos naturales de los que provienen y, en consecuencia, el aumento continuo de las emisiones de dióxido de carbono (CO_2) a la atmósfera están intensificando la búsqueda de la conversión del dióxido de carbono a combustibles y químicos de valor agregado, el objetivo principal es reducir las emisiones y crear fuentes de energía renovables y sostenibles. Es un tema muy activo en el área de investigación y desarrollo, hay mucho interés en la reducción fotocatalítica de CO_2 con H_2O, principalmente empleando energía solar, la cual es una fuente renovable con suministro de luz continuo y fácilmente disponible. El progreso reciente en esta área se ha centrado en el desarrollo de fotocatalizadores prometedores, primordialmente basados en TiO_2. En este contexto, este artículo analiza (i) el papel del CO_2 en el tratamiento de problemas relacionados con la energía y el calentamiento global, (ii) el conocimiento fundamental de la reducción fotocatalítica de CO_2, (iii) el papel de los catalizadores de TiO_2 dopados con cobre en la transformación fotocatalítica de CO_2, así como (iv) oportunidades emergentes y cruciales para la investigación futura empleando fotocatalizadores con Cu-TiO_2, haciendo mención de las referencias relevantes más actualizadas.

CO_2, reducción fotocatalítica, Cu-TiO_2

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Introduction

It is well known that global warming has become a serious problem for the ecological balance of planet Earth, since due to this phenomenon, the climate of each of the existing ecosystems has changed; giving rise to major meteorological anomalies such as hurricanes, tornadoes and droughts; as well as the destruction of ecosystems (extinction of species), melting of the polar ice caps, floods, among others. This phenomenon is caused by the greenhouse effect, a natural mechanism by which the planet's atmosphere stores heat from the sun, as well as an excessive deforestation occasioned by population growth that requires greater consumption of food and habitable places (Tan, Lu, Xu, & Luo, 2012). The greenhouse effect is due to the presence of some gases that can absorb a large amount of the energy emitted by solar radiation, known as greenhouse gases (GHG). These gases, such as carbon dioxide (CO_2), water vapor (H_2O), methane (CH_4), ozone (O_3), nitrogen oxides (NO_x), chlorofluorocarbons (CFCs) contribute significantly to the global warming of the atmosphere (Ganesh, 2016); the energy in the form of light and radiation coming from the sun, which bounces off the earth's surface and should go out into space, does not return completely because pollutant gases avoid that, and they return part of this energy to the surface, similar to the walls of a greenhouse look like (Ming, De Richter, Liu, & Caillol, 2014). Between these gases, CO_2 and water vapor are found in greater quantity in the atmosphere, that is why they are considered the main cause of this warming (Ambrožová et al., 2018; Singhal, Ali, Vorontsov, Pendem, & Kumar, 2016b; Tasbihi et al., 2019; Vu, Nguyen, Kaliaguine, & Do, 2017). Since 1750, anthropogenic activities have produced an increased in atmospheric carbon dioxide concentrations by 40%, from 280 ppm in 1750 to around 400 ppm in recent years, and it is very likely that this will continue to increase in the forthcoming years since developing countries are still moving forward of industrialization (Singhal et al., 2016b; Tasbihi et al., 2018). It was even predicted that the CO_2 content could reach 750 ppm and the global average temperature could rise between 5.5 and 8.3°C (Shehzad, Tahir, Johari, & Murugesan, 2018).

In this regard, at the international level, various actions in various agreements such as the Kyoto Protocol have been taken, the Copenhagen Agreement and the Cancun Agreements of the United Nations Framework Convention on Climate Change (UNFCCC), the organ of the Organization of the United Nations (UN) responsible for the climate on the planet. All those efforts, taken together, laid the foundation for the 2015 Paris Climate Change Conference, which is officially known as the 21st Conference of the Parties (COP21) to engage nations to work together and reduce CO_2 emissions by 50%, also to limit the increase in the global average temperature to less than 2ºC, by the year 2050. In order to achieve this objective, the reduction of CO_2 emissions is mandatory. The development of alternative energy sources to replace fossil fuels is mainly focused on the development of cleaner energy sources, without carbon emissions, such as turbines driven by water and wind and solar energy, the problem with these renewable energy sources is the intermittent nature of the energy produced (Mebrahtu et al., 2019). Furthermore, there is an urgent need to find a solution to mitigate, store or convert the CO_2 produced or emitted in order to keep the level of atmospheric CO_2 at least constant (Singhal et al., 2016b). Although there are several applications for this greenhouse gas, the amount used is minimal and does not contribute to decrease the amount of gas present in the atmosphere. Urea, salicylic acid and polycarbonates, ethylene, propylene, carbonates and polycarbonates are some of the compounds currently produced from CO_2 (Centi & Perathoner, 2009), in addition, it is used as a refrigerant in the preservation of food, a carbonating agent in beverages, a supercritical solvent, as inert medium, and a pressurizing and neutralizing agent (Ganesh, 2016).

Between strategic routes proposed to maintain the level of CO_2 emissions are:

1) Mitigation of CO_2 emissions,

2) Capture and storage of CO_2 (CCU) and,

3) CO_2 transformation.

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Concerning mitigation of the CO_2 emissions, different actions pursue to minimize them. Among these actions are the establishment of environmental regulations and the limitation of vehicular circulation, amongst others applicable for discharges that come from large facilities for instance the cement, metal, bioethanol, oil refining and petrochemical industries, power plants for the production of electricity, medium sources such as industrial and commercial buildings and from small sources such as transport. These actions have been insufficient though, because it is also necessary to improve energy efficiency and promote the use of renewable energy (Li et al., 2018). As for the second strategic route, its goal is to generate value-added chemical products, its importance lies in the fact that it can alleviate the dependence on fossil fuels to produce energy and at the same time promote technical sinks in the carbon cycle; its disadvantages are that the process generates high costs associated with the storage, transportation and consumption of energy. For now, new technologies for capture and sequestration (CCU) are being developed in saline aquifers, in oil and gas fields, and the use of mineral carbonation technology in situ. For the third and final strategy, there are great challenges to convert CO_2 into fuels and value-added chemicals, mainly because its conversion to carbon-based fuels requires a large amount of energy to break the bond since the molecule is chemically stable due to its carbon-oxygen bonds (C=O bond enthalpy of +805 kJ/mol). The environmental and economic benefits can be very favorable, using biological reduction, electrochemical reduction, photo-reduction catalytic, thermo-catalysis, photo-electroreduction, etc. (Ganesh, 2016; Ola, Maroto-Valer, & Mackintosh, 2013).

Biological and photo-electrocatalytic processes are at an earlier stage, particularly, which need to be studied for a medium and long term. The photocatalytic reduction of CO_2 into renewable fuels and chemical products is considered a viable path for sustainable development and to alleviate both problems, environmental and energetic, because it can use solar energy to reduce atmospheric or sequestered CO_2 and at the same time generate useful chemicals as sources of energy (Tasbihi et al., 2019; Xiong et al., 2018).

From recent research results, CO_2 can be used to produce methanol from synthesis gas (a mixture of carbon monoxide and hydrogen $CO+H_2$) using it instead of CO. In the reduction of CO_2 through various synthesis routes, the formation of fuels such as ethanol, methane or hydrogen, and of other short-chain organic chemicals such as methanol, formaldehyde and acetic acid and even formic acid have been observed, although this last is generated mainly through electro-reduction.

The main variables that determine the selectivity towards some of these products, during CO_2 reduction, are the nature of the catalyst in the case of photo-reduction, the electrodes in the case of electro-reduction and photo-electroreduction, in addition to the reducing agent and the configuration of the reactor.

The objective of this review is to analyze some of the basics and results reported in the literature regarding the carbon dioxide conversion photocatalyzed by Cu and TiO_2-based materials. Therefore, in the first section the basics of heterogeneous photocatalysis is given and in the next section the catalysts used to conduct the reduction of CO_2 by photocatalysis, are summarized. In the other sections, the most studied variables, are analyzed and the results are presented.

Heterogeneous photocatalysis: overview

Chemical reactions are classified in various ways, the scheme that facilitates the design of chemical reactors is to consider the number of phases that are implicit in the reaction, resulting in the classification of homogeneous and heterogeneous reactions. There is a homogeneous reaction when it is carried out in the presence of a single phase, when there are two or more phases it is a heterogeneous reaction (Levenspiel, 1998). The catalyst, according to the International Union of Pure and Applied Chemistry (IUPAC), is a material that modifies the speed of a reaction and does not alter the Gibbs free energy in the reaction; another of its characteristics is that it can be recovered after each catalytic cycle, in addition to the fact that it does not affect the equilibrium configuration of the original reaction system.

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The main characteristics of a good catalyst are activity and selectivity, together with reproducibility, thermal and mechanical stability, and the ability to be easily regenerated. One of the pillars of modern chemical and energy industries is heterogeneous catalysis, whereby a reaction in the gas or liquid phase is carried out on a solid catalyst, the design of active and robust catalytic processes is the ultimate goal. When the suspension of a particular catalyst (generally semiconductor materials) is irradiated with natural or artificial light, the process is known as heterogeneous photocatalysis. Unlike "conventional" catalysis (using transition metals, organocatalysis, or Lewis acid catalysis), photocatalysis proceeds through the transfer of electrons or energy to generate reactive substrates or reagent intermediates rather than reducing the transition state energy. For nearly fifty years, redox photocatalysis has found widespread utility in the areas of carbon dioxide reduction, water splitting, and solar cell materials.

Ideally, the design of materials that have self-regeneration of active sites is sought for critical catalytic processes such as biomass improvement, CO_2 reduction and light activation of alkanes. This is due to the increasing demand for energy, chemicals, food and also to the worldwide increase in anthropogenic CO_2 emissions.

Photocatalysis is a process that is based on the direct or indirect absorption of visible or ultraviolet radiant energy by a solid photocatalyst, generally a semiconductor. When the photocatalyst is irradiated with light that has an energy greater than the energy of the bandwidth of the photocatalyst (band gap), the semiconductor absorbs the photons, which are excited and are promoted from the valence band (BV) to the conduction band, (BC), generating positive holes (h^+) and electrons (e^-). The generated holes (h^+) can oxidize electron donors, while electrons in BV are capable of reducing electron acceptors through single electron transfer. Then, a photocatalyst is a substance that can be activated by the adsorption of a photon increasing the reaction rate without being consumed. This material should be a semiconductor.

The excited electrons, in the photocatalytic process, are transferred to the reducible species, while the catalyst accepts electrons from the oxidizable species that will occupy the holes. In this way, the net flow of electrons will be zero and the catalyst remains unaltered, in other words, the electrons and holes react until reaching a steady state when the disappearance of electrons and holes is equal to the speed of generation of electrons and holes due to lighting (Hurtado, Natividad, & García, 2016). Therefore, for photocatalysis to take place, three components are necessary:

a. photons emitted with an appropriate wavelength,

b. catalytic surface of a semiconductor, and

c. the oxidizing or reducing agent.

Photocatalysts for CO_2 reduction

Since Inoue et. al. published the first report on the photo-reduction of CO_2 in organic compounds, in 1979, a great variety of photo-catalysts have been developed and studied for the photo-reduction of CO_2 (Olowoyo et al., 2018; Shi et al., 2018; Vu et al., 2017). There are different types of semiconductors; however, not all of them can be used in photocatalytic reactions. It has been reported that the most appropriate photocatalysts must be stable both in chemical terms and with respect to lighting and without toxic constituents, in addition, the type of chemical species to be oxidized or reduced must be considered. Metal oxides are widely accepted as photocatalysts due to their semiconducting nature and the possibility of doping their structure to reduce the bandgap energy or to efficiently separate the hole-electron pairs.

During the last years, the photocatalytic conversion of CO_2 has been studied using many types of photocatalysts such as ZnO, ZrO_2, Al_2O_3, TiO_2, Fe_2O_3, $ZnFe_2O_4$ and SiO_2, among many others (Artz et al., 2018; Ola & Maroto-Valer, 2015; Sohn, Huang, & Taghipour, 2017). However, the quantum efficiency and yields of the products in photocatalytic CO_2 reduction remain low and require further study (Halder et al., 2018).

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Among the most extensively investigated photocatalysts, and one of the most important semiconductors in photocatalysis is titanium dioxide (TiO_2), most of the research on the photo-reduction of CO_2 is linked to this material, this is due to its numerous advantages including low cost, high availability, zero toxicity, long-term stable (against photo-corrosion and chemical corrosion), thermally stable, antibacterial effect, and strong oxidative potential under lighting (Sohn et al., 2017). However, although TiO_2 has several unique properties, its practical application is limited due to its low quantum yield, and its energy bandgap (for the anatase phase 3.2 eV, rutile 3.0 eV and brookite 3.4 eV). The low photoactivity is due to the fact that this material can only be excited with light with an energy greater than 3.2 eV; that is, radiation at a wavelength of 380 nm or less (ultraviolet light) is required, which represents between 2 and 5% of solar radiation; the other challenge is to improve the useful life of the hole-electron pairs, which is very short (Edelmannová et al., 2018; Tahir, Tahir, Aishah, Amin, & Alias, 2016); that is, after excitation (arrow 1, Figure 1) there is a rapid recombination of the photogenerated charge carriers from the valence band towards the conduction band (the e^- electron returns from the conduction band to the h^+ hole formed in the valence band rapidly (arrow 2, Figure 1); both disadvantages, bandgap and rapid recombination, directly affect catalytic efficiency.

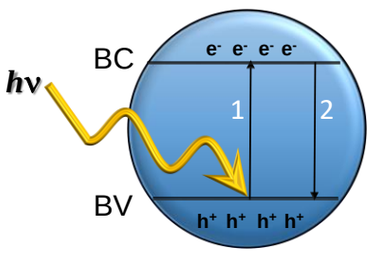

Figure 1. Schematic representation of the recombination of the hollow-electron pair (h^+ - e^-) in a photo-excitation process (BC: conduction band, BV: valence band)
Source: "Elaborated by the author"

Due to this fact, studies are carried out so that TiO_2 can be activated in the visible light spectrum with modifications of optical and electronic properties to include a decrease in bandgap and increase the useful life of the hollow-electron pair (suppression of recombination).

The photocatalytic activity of TiO_2 towards visible light can be increased by doping it with organic and inorganic compounds such as photosensitizers, combining semiconductors with different energy levels (Edelmannová et al., 2018; Singhal et al., 2016b), or by doping metals and non-metals. These modifications are necessary to trap the hole or the electron to carry out the desired reaction, thus, the electronic trap photo-generated by metal impregnated on the surface of the semiconductor can delay the recombination process. Noble metals are generally used as co-catalysts (Ni, Shen, Li, Ma, & Zhai, 2017), serving as electron traps to suppress the recombination rate of photogenerated charges. Au, Ag, Cu, Ni, and especially Pt are considered efficient in improving the photoactivity and selectivity of TiO_2 in the sunlight spectrum. In this sense, copper has been reported as an efficient dopant to improve the photo-activity of TiO_2 in the selective reduction of CO_2, copper has attracted attention due to its economic viability and high availability, low toxicity and good photo-activity.

Photocatalytic reduction of carbon dioxide with TiO_2 doped with copper

The incorporation of copper ions (Cu^0, Cu^+, Cu^{2+}) in TiO_2 could lead to stimulate the transfer of electrons between the metal / semiconductor junction to improve photo-activity (Jin, Luo, Zan, & Peng, 2017; Ratcliff et al., 2018). Specifically, copper oxide (CuO) has become interesting for the formation of photocatalysts with heterojunction structures due to its availability, good stability and its absorption of visible light; is a typical p-type semiconductor compound with a monoclinic structure and narrow bandgap (E_{bg} = 1.2 - 2.0 eV), it has exhibited a wide range of potential technological applications such as biosensors, gas sensors, electrode materials, superconductors, photovoltaics, photoconductors and photocatalytic uses. Inserting CuO into the TiO_2 structure can cause an increase in photocatalytic activity, because an internal electric field is created, which promotes separation of electron holes and slows down the recombination of the charge carrier. In the presence of an electron donor (reducing agent), the CO_2 reduction reaction is performed instead of the hollow-electron pair recombination (Figure 2).

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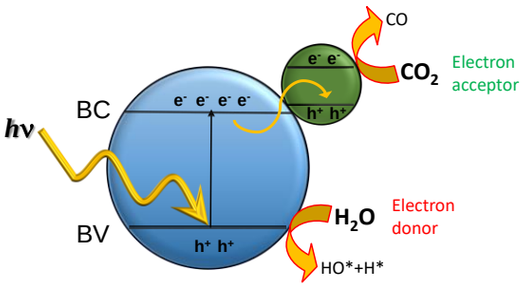

Figure 2 Schematic representation of the deceleration of the recombination of the hollow-electron pair in TiO_2 (blue sphere) by means of the introduction of copper species (green sphere) in its structure (for the generation of CO) (BC: conduction band, BV: valence band)
Source: "Elaborated by the author"

In general, copper species that act as co-catalysts have been incorporated into TiO_2 by impregnation, microemulsion, sol-gel, and plating methods. Active species and their sizes are difficult to control during the synthesis and its treatment processes, therefore, the optimal amount of Cu loading varies from one methodology to another, and the active species are still under investigation (Ni et al., 2017).

Although many studies have reported that co-catalysts are capable of improving the photocatalytic efficiency of TiO_2, mainly in wastewater treatment or in advanced oxidation processes, their effect on the selectivity of the product in the reduction of CO_2 is still debated (Xiong et al., 2017) as well as the reaction mechanisms (Kavil et al., 2017). The possible products of the reduction and oxidation reactions in the photoconversion of CO_2 with water are: methane, methanol, hydrogen, ethanol, formaldehyde and / or formic acid (Cheng, Yang, Chen, Zhu, & Liao, 2017) although ethylene has also been reported in other processes (Ola & Maroto-Valer, 2015). Table 1 contains a short list of possible reactions (conditions: pH 7, 1 atm, 25 ° C).

Reacción
$TiO_2 + hv \rightarrow e_{cb}^- + h_{vb}^+$ (1)
$2H_2O + 4h_{vb}^+ \rightarrow O_2 + 4H^+$ (2)
$CO_2 + 2H^+ + 2e_{cb}^- \rightarrow HCOOH$ (3)
$CO_2 + 2H^+ + 2e_{cb}^- \rightarrow CO + H_2O$ (4)
$CO_2 + 4H^+ + 4e_{cb}^- \rightarrow HCHO + H_2O$ (5)
$CO_2 + 6H^+ + 6e_{cb}^- \rightarrow CH_3OH + H_2O$ (6)
$CO_2 + 8H^+ + 8e_{cb}^- \rightarrow CH_4 + H_2O$ (7)

Table 1 CO_2 photoreduction reactions

In general, several steps of synergistic transfer of protons and electrons (possessing individual activation energies) must be accomplished, and this is where the challenge lies in the design of the catalyst and the diverse combination of process variables in order to increase performance and induce selectivity towards some of the products.

Next, a condensate of some of the investigations carried out in recent years in which copper precursors supported on various materials have been used to carry out the photoreduction of CO_2 is presented. In Table 2, it can be seen that various combinations of technology have been assessed to achieve a common goal, the reduction of CO_2. Likewise, Table 2 lists investigations that have used catalysts with copper in their structure.

In the first place, in terms of the methodology to support Cu compounds in different supports, each investigation differs; even, in the same research, various methodologies for the preparation of catalysts with copper are reported, like in Nogueira et al., 2020, or variables that influence their preparation are still studied, such as in Camarillo, Tostón, Martínez, Jiménez, & Rincón, 2018. Nogueira et al., 2020 reported the preparation of its CuO nanoparticles by three different techniques: solvothermic, coprecipitation and direct calcination, obtaining the highest methane production with solvothermal synthesis. Camarillo et al., 2018 used a hydrothermal technique with two titanium precursors (titanium tetraisopropoxide and diisopropoxytitanium bis-acetylacetonate), two alcohols (ethanol and isopropanol) and a copper precursor (Cu (II) acetylacetonate), the catalysts produced showed better catalytic activity compared to the commercial reference catalyst Degussa P-25, in addition to the methane and CO production rates obtained with TTIP-isopropanol-Cu 1% by weight (1.493 µmol / gh and 9.913 µmol / gh, respectively).

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Catalyst	Reductor	Reaction products		Reference
CuO	H_2O	Methane	16.7 µmol/ g h	Nogueira et al., 2020
Cu/TiO_2	KOH 0.2M	Methane Ethylene Methanol Acetone	0.3 µmol/g h 0.04 µmol/ g h 19.7 µmol/ g h 31 µmol/ g h	Olowoyo et al., 2018
Cu(II) tetra(4-carboxylphenyl) porphyrin/ TiO_2	Water steam	Methane CO	16 µmol/g h 3 µmol/g h	Wang et al., 2018
CuO/ TiO_2 powder	H_2/ H_2O	Methane CO	7 µmol/g 35 µmol/g	Edelmannová et al., 2018
CuO/ TiO_2 powder	H_2O	Methanol Methane	47 µmol/ g h 3 µmol/ g h	Spadaro, Arena, Negro, & Palella, 2018
CuO/ $NaTaO_3$	Isopropanol	Methanol	1322 µmol/ g h	Xiang et al., 2018
Cu nano-particles/ g-C_3N_4 nano-sheets	$KHCO_3$ 0.1M	CO	49.43 µmol/g	Shi et al., 2018
Pt/TiO_2 Cu/TiO_2 powder	NaOH 0.2M	Methane H_2 CO	2 µmol/ g h 13.8 µmol/ g h 1 µmol/ g h	Ambrožová et al., 2018
Cu (Sn)/TiO_2 Cu (NH_3)/TiO_2 nano-composites	Water steam	CO	0.9 µmol	Deskins, 2018
Cu/TiO_2 (Cu $^{2+}$ and CuO) powder	NaOH 0.2M	Methane H_2 CO	2.5 µmol/g h 2.2 µmol/g h 1 µmol/g h	Tasbihi et al., 2017
Cu/TiO_2 nano-particles	Water steam	Methane CO	1.5 µmol/g h 9.9 µmol/g h	Camarillo, Tostón, Martínez, Jiménez, & Rincón, 2018
Cu-C/TiO_2 nano-particles, C/TiO_2, P-25	NaOH 0.2M	Methanol	518 µmol/g h	Kavil et al., 2017
Cu/Pt–$HCa_2Ta_3O_{10}$ Perovskyte nano-sheets	Water steam	Ethanol Methanol	113 µmol/g h 7.4 µmol/g h	Vu, Nguyen, Kaliaguine, & Do, 2017
Cu^{2+}-TiO_2 (TiO_2 nano-tubes)	Water steam	Methanol Ethanol	36.1 µmol/g h 79.1 µmol/g h	Cheng, Yang, Chen, Zhu, & Liao, 2017
Pt and Cu_2O NPs/ TiO_2 nano-crystals	Water steam	Methane CO O_2	0.99 µmol/g 0.4 µmol/g h 2.2 µmol/g h	Xiong et al., 2017
Cu-TiO_2	H_2O / Na_2S	Hydrogen CO HCOOH	313.2 µmol/ g h 2.8 µmol/ g h 25.7 µmol/ g h	Gonell, Puga, Julián-López, García, & Corma, 2016
Cu-NPs/TiO_2	Water steam	Hydrogen CO HCOOH	452 µmol/g h 334 µmol/g h NC	Singhal, Ali, Vorontsov, Pendem, & Kumar, 2016
Cu_2O/ Graphene multilayer	H_2O (pH 12)	Hydrogen Ethanol O_2 HCOOH	2031 µmol/g h 545 µmol/g h traces traces	Hurtado, Natividad, & García, 2016
Cu / ZnO / TiO_2	NaOH 0.2M	Methane	153 µmol/g	Paulino, Salim, & Resende, 2016

Table 2 Recent research on photocatalytic reduction of CO_2 using catalysts with Cu and TiO_2

Other synthesis methods reported are sono-hydrothermal (Olowoyo et al., 2018), incipient impregnation (Gonell et al., 2016; Spadaro et al., 2018), in-situ reduction (Jiang, Katsumata, Hong, Yamaguchi, & Nakata, 2018), hydrothermal microwave (Camarillo, Tostón, Martínez, & Jiménez, 2017; Shi et al., 2018), calcination-reduction (Singhal et al., 2016a) and one of the most reported, the sol-gel method (Ambrožová et al., 2018; Kavil et al., 2017; Ratcliff et al., 2018; Tasbihi et al., 2017).

In 2013, Kondratenko, Mul, Baltrusaitis, Larrazábal, & Pérez-Ramírez reported that the preparation of Cu-promoted TiO_2 catalysts greatly affects performance: impregnation leads to less active materials compared to those prepared by sol-gel methods, with methanol being the main product. However, a direct relationship between the method of preparation and the yield or selectivity towards some of the products formed is still uncertain.

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The copper loading has been one of the most studied variables, with a loading from 0 to 5%, observing that when a greater amount of copper is deposited, the catalytic activity is lower (Tasbihi et al., 2017). Camarillo, Tostón, Martínez, & Jiménez, 2017 reported that the best methane and CO production rates were obtained with a 1% Cu loading and not with a 3%. It has been shown that Cu species have a high capacity to absorb CO_2 molecules to facilitate their subsequent activation and avoid reoxidation, thereby increasing methane production. Cheng et al., indicate that the methanol and ethanol yields increased with the Cu^{2+} load, but decreased when the concentration exceeded 0.02M (1.5% wt). Ratcliff et al., 2018 reported the best catalytic activity towards CO with a load of 3% Cu/TiO_2. The decrease in the photocatalytic activity of Cu/TiO_2 with high Cu loading is probably due to the decrease of the active sites of the surface due to an excessive deposition of Cu clusters, although these Cu clusters can act as the recombination centers for holes and electrons (Ni et al., 2017), a total dispersion in the TiO_2 is required for the light to pass through the catalyst.

Regarding the reducing agent, copper-containing catalysts have been used in both liquid and gas phase reactions (hydrogenation); hydrogenation of carbon dioxide to hydrocarbons is possible, but requires a high consumption of H_2 and therefore is less interesting. In liquid phase, the most preferred reducing agent is water or water vapor, although water is an ideal electron donor, the reduction of CO_2 by water is less favorable and slower than the photocatalytic reduction of water to hydrogen, since the reduction potential from H_2O to H_2 is much smaller than the reduction potential from CO_2 to CO^{2-} and CO_2 reduction requires 6-8 e^- with more negative reduction potential than just the 2 e^- required for water reduction to generate H_2 (Camarillo et al., 2017). There are various authors such as Ambrožová et al., 2018; Kavil et al., 2017; Olowoyo et al., 2018; Shi et al., 2018; Tasbihi et al., 2017 who opted for the use of alkaline solutions rather than only water, due to the benefit provided by the use of hydroxide salts by increasing the amount of substrate in solution (CO_2) in the form of carbonate or bicarbonate ions.

Olowoyo et al., 2018 studied the effect of different bases including K_2CO_3, Na_2CO_3, NaOH, KOH and the base concentration; the best catalytic performance (19.6 µmol/g h of methanol) was observed with the use of 0.2M KOH. Kavil et al., 2017 also studied the effect of the addition of NaOH on the yield of the methanol produced, it was observed that the formation of methanol under alkaline conditions was greater than under acidic or neutral conditions, the highest yield of methanol (518.6 µmol/g h) was obtained with the 0.2M NaOH solution.

Finally, the content of the reaction products column in Table 2, which is the one of greatest interest due to its relationship with the main topic of this publication: the formation of organic chemical products. It should be noted that there has been a greater focus on products generated in the gas phase such as: methane, methanol, hydrogen, CO; and not towards the possible products that could be reduced or found in the liquid phase such as: formic acid, acetic acid, formaldehyde, methanol, ethanol. There are few publications reporting production of formic acid by photocatalysis, although, there is large interest on the conversion of carbon dioxide to formic acid, but the availability of efficient technologies to use formic acid as energy carrier, as well as the toxic character of formic acid limit the attention. Singhal et al., 2016b carried out the photo-catalytic division of formic acid to confirm that the generation of hydrogen comes as a result of the photo-catalytic division of acids/formic formats formed during the reduction of CO_2 and that it is also related to the reduction of CO_2 to CO. Ratcliff et al., 2018 detected as the main product CO and a small amount of CH_4, the decrease in methane prduction over time was attributed to a possible oxidation with O_2 towards CO_2. Slamet et. al. found that the photocatalysis promoted by CuO showed a better performance than the materials promoted by the species Cu^0 and Cu^{+1} (Olowoyo et al., 2018). Ratcliff et al. stated in 2018, that Cu based catalysts prevail in their studies due to their high selectivity and fewer undesired by-products. Kavil et al., 2017 reported the formation of methanol by TiO_2 photocatalysts in a CO_2 and H_2O system, the formation of the alcohol was quite high on $Cu\text{-}C/TiO_2$ compared to that on both $P25\text{-}TiO_2$ and C/TiO_2.

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The performance of the products in the photocatalytic reduction of CO_2 remains low and requires more studies, Cheng et al., 2017 reports that their yields were improved with the increase in the reaction temperature, since the photocatalytic reduction of CO_2 and water vapor is an endothermic process and therefore higher temperature can accelerate the reaction rate naturally, furthermore, increasing the temperature is beneficial for the desorption process of the products from the surface of the photocatalyst. On the other hand, regarding the reaction mechanism on the Cu-TiO_2 catalytic surfaces, it has been reported that the photocatalytic CO_2 reduction process begins with the adsorption of CO_2 molecules on the surface of the Cu/TiO_2 photocatalyst, and can take place on the TiO_2 photocatalyst surface, the Cu surface or at the Cu-TiO_2 interface (Singhal et al., 2016a) and that the next step is the dissociation of the HOCO to separately form the adsorbed hydroxyl group and the carbon monoxide; however, it has not yet been proven and remains a limited and controversial topic.

Therefore, various combinations can still be made to improve selectivity, yield, and understand or demonstrate the reaction mechanism for photocatalytic transformation of CO_2, which is still a subject of study and debate.

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Conclusions

The area of research on the conversion of carbon dioxide into valuable fuels and chemicals remains very popular. This article recognizes the use of CO_2 as a direct raw material to produce fuels via photocatalytic reduction on different species of copper over TiO_2 synthesized in different ways, with different copper contents on the support and different reducing agents. There is still limited information on how these aspects affect the yield and selectivity of the reaction. This review briefly analyzes the current state of art of various options for converting carbon dioxide into fuel with an emphasis on photocatalytic aspects using photocatalysts containing copper on titanium dioxide.

This review of the literature reveals that there are still imprecise aspects of the use of copper in TiO_2 substrates; further research to understand the impact of operating conditions on the photocatalytic reaction may be helpful for photocatalyst design, process optimization, and photoreactor design parameters. The use of copper-TiO_2 induced photocatalysis for complex CO_2 conversion remains a promising path, as this catalyst can be activated by solar energy under relatively mild conditions to form valuable products. Despite recent advances, the expected improvement required for scalable fuel production has yet to be achieved. For this reason, the development and synthesis of new photocatalysts with greater stability, selectivity and efficiency require improvements in the synthesis processes that allow a better control of the physicochemical properties of the photocatalyst, the implementation of analytical methods such as spectroscopy of surface area and volume is also of great importance to obtain valuable information on the main stages of photocatalytic CO_2 reduction and to understand in more detail the reaction mechanism: limiting reaction rate steps, formation and stability of intermediate reaction products on the surface, adsorption and desorption of reactants and products and in this way propose the modification of photocatalysts and the design of photoreactors that play a fundamental role in the overall performance of the process.

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