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Applications of supercritical technologies to CO_2 reduction: Catalyst development and process intensification

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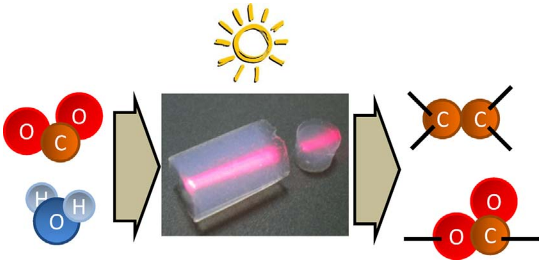
GRAPHICAL ABSTRACT



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ABSTRACT

Our economy relies on fossil fuels that can be converted into energy and chemicals, but this model is endangered by depletion of resources and environmental problems. To solve this dilemma, we can find inspiration in photosynthetic organisms that consider CO_2 as a carbon source and not as waste. CO_2 utilization processes have experienced a considerable development, but they still face important limitations, regarding complexity, productivity and cost. To overcome these limitations, research is being carried out in the development of catalysts with enhanced activity and durability, and on process intensification and optimization of the energy delivery to the system. In this article, the applications of supercritical fluids in this important research field are reviewed, focusing on CO_2 reduction processes by photocatalytic, electrochemical or hydrothermal methods Two key research areas are described: the development of catalysts with supercritical fluid processes, and reactor intensification by application of pressurized conditions and supercritical fluids.

1. Introduction

There is an increasing global concern about the negative effects of climate change, which are related to the increasing concentration of greenhouse gases in the atmosphere, and in particular CO_2, due to the use of fossil fuels. The recent Paris Agreement, set in 2015, has as its main objective the reduction of CO_2 emissions in order to avoid a global temperature increase higher than 2 °C. To attain this objective, it is necessary to gradually replace fossil fuels by renewable energies with zero CO_2 emissions, but it can be expected that fossil fuels will remain as the main energy source for many years, particularly for production of electricity and as fuels for vehicles. Therefore, other solutions such as carbon capture and storage (CCS) technologies must be considered, because they would enable a significant reduction of the CO_2 emissions of thermal power plants or chemical industries such as the industries of production of ammonia, hydrogen and cement [1].

Different CO_2 capture technologies have been researched. Among them, the most developed technology at industrial level is the absorption using aqueous solutions of alkanolamines, a method that has been used since the 30 s to remove CO_2 and other acid gases from natural gas

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[2]. Alkanolamines such as monoethanolamine (MEA), diethanolamine (DEA) and methyldiethanolamine (MDEA) selectively and reversibly react with CO_2 forming carbamates, and can capture 0.5–0.7 mol CO_2/mol amine [3,4]. However, the heat of absorption is high, implying that the amine regeneration step, which is carried out by desorption at temperatures of 100–150 °C, has high energy consumption. Alternative absorption processes for CO_2 capture processes have been developed, such as the “Chilled Ammonia” process presented by the French company Alstrom [5]. This method uses an aqueous ammonia solution at low temperature (2–10 °C), where CO_2 is absorbed as ammonia carbonate, bicarbonate and carbamate. Typically, 0.33–0.67 molCO_2/molNH_3 can be absorbed. As in the case of amines, regeneration is carried out by desorption at temperatures of 100–150 °C and pressures of 2–136 bar. Compared to the case of amines, the heat of desorption from the ammonia solution is much lower, which implies that the energy costs of the regeneration also are lower. The disadvantage of this method is the need of big amounts of refrigeration water. For this reason, in general this method is only considered for facilities located near the sea.

Besides these absorption methods, other CO_2 capture technologies are being developed, such as adsorption of membrane separation [6]. In general, all these processes are costly, because in addition to the cost of the CO_2 separation process, the cost of compressing and transporting CO_2 to the storage site is also high. In fact, it has been estimated that even employing favorable technologies for CO_2 separation such as oxy-fuel combustion, the incorporation of a CO_2 capture and storage unit in a thermal power plant implies a significant penalty on the global efficiency of the plant, which is estimated as 2–3% of the global efficiency of the power plant [7], a penalty that is assumed estimating that the benefits of reduced CO_2 emissions outweigh it.

Therefore, it can be concluded that CO_2 capture is a complex and costly process, which justifies the general appreciation of CO_2 as a problematic residue that causes considerable economic problems and environmental harms. In contrast, looking into nature, carbon dioxide is the basic chemical resource used by plants. By transforming it into chemical fuels, they store surplus solar energy for periods of need. By converting it into complex organic compounds, they obtain the building blocks that they need to grow and live. A similar approach can be followed in the industry, converting CO_2 in valuable compounds that can generate a profit instead of simply storing it [8]. Furthermore, it must be considered that fossil fuels not only provide most of the energy we use, but also are the main raw material used by the chemical industry. Therefore, it is necessary to find an alternative of base compounds for the chemical industry that can gradually replace the compounds obtained from fossil fuels as they run out. CO_2 utilization technologies can also contribute to this purpose, because they can produce important platform chemicals such as formic acid or methanol, and CO_2 is a widespread resource that can contribute to the creation of a novel decentralized industrial structure that produces “just enough” [9].

Following this approach, different Carbon Capture and Utilization (CCU) technologies are being researched [10]. Among other options, four key CO_2 conversion technologies are being intensively studied: (1) catalytic copolymerization of CO_2, particularly with highly reactive epoxides for the synthesis of polycarbonates [11]; (2) thermo-catalytic CO_2 conversion processes [12,13]; (3) CO_2 fixation in photo-bioreactors [14]; and (4) photocatalytic CO_2 conversion processes, also known as “artificial photosynthesis” methods [15]. The application of supercritical fluids can contribute to the development of these technologies in several aspects such as materials design, process intensification and reaction engineering. The objective of this article is to present an overview of the recent progress and the perspectives in the application of supercritical fluids in carbon dioxide reduction, focusing on two key areas: catalyst development and process intensification. Since the production of carbonates or polymers by reaction between CO_2 and epoxides and related compounds is discussed in another article of this special issue, this application will not be considered in this article.

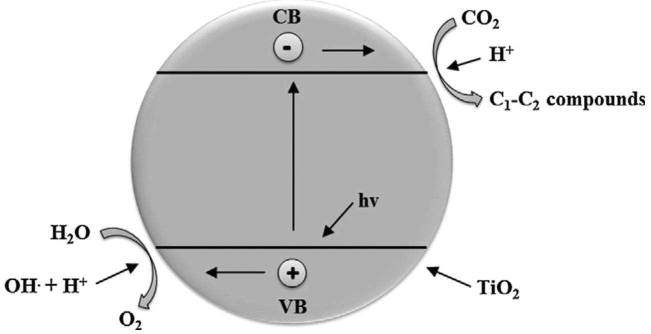

Fig. 1. Schematic representation of the reaction mechanism of the photocatalytic CO_2 reduction over a semiconductor particle. Figure reproduced from [17]. Figure distributed under the terms of the Creative Commons License (CC BY 4.0).

2. Applications of supercritical fluids for the production of catalysts for artificial photosynthesis

The origin of “artificial photosynthesis” systems is usually tracked back to the seminal work of Fujishima and Honda, who in 1972 demonstrated the photoelectrochemical splitting of water using a single-crystal TiO_2 photoanode and a Pt cathode with an external electrical bias [16]. Following this work, a considerable work has been carried out in the development of photoelectrochemical and photocatalytic CO_2 conversion systems, and particularly in the development of suitable photocatalysts, which are an essential element of these systems.

The photocatalysts employed are materials that are able to absorb light energy, generating free electrons (e-) and holes (h’), as shown in Fig. 1 [17]. Some of the most employed materials are TiO_2 and other semiconductors. The photo-induced electron-hole pairs produced in these materials can initiate the redox reactions required to convert CO_2. Therefore, a fundamental aspect determining the photocatalytic activity of the material is the efficiency of stabilization of the charge separation induced by light excitation. Charge separation can be enhanced adding metal co-catalysts to the material, such as Pt, that actuate as sinks for the free electrons produced. Such semiconductor-cocatalyst systems are some of the most promising photocatalytic materials for water splitting and CO_2 reduction available today [18]. Charge separation can also be stabilized by geometrical factors, producing catalysts with appropriate and controlled (nano) sizes and shapes [19]. Following this approach, different (and, in some cases, patented) designs describe nano-structured materials with a high aspect ratio (length/width, e.g. fibers or rods), including: TiO_2 nanofibers [20], TiO_2-coated ZnO nanorods deposited over a silicon substrate [21], or a double-layer structure, formed by Si nanowires vertically disposed over the two sides of a PEM membrane [22] (Fig. 2). Moreover, the range of light wavelengths in which the photocatalytic material is active is an extremely important property. Ideally, the material should have a maximum activity in the visible light range, but commonly used semiconductor photocatalysts, such as commercial TiO_2, show their maximum activity in the UV range. The development of photocatalysts suitable for light absorption in a wide wavelength range is extremely challenging, because light absorption depends on many factors, including the chemical composition, the crystalline structure and type and density of defects, the particle size, or the interactions at the interface between the photocatalyst and the co-catalyst. It is therefore necessary to develop a method for production of the catalyst that can control all these aspects. Considering the possibilities of supercritical fluid technologies for the development of such materials with tailored properties, several researchers have studied the production of photocatalysts in supercritical media.

As previously described, semiconductor-cocatalyst photocatalytic