



Review

Recent advances in the photocatalytic conversion of carbon dioxide to fuels with water and/or hydrogen using solar energy and beyond

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ABSTRACT

Photocatalytic reduction of carbon dioxide to fuels using solar energy is an attractive option for simultaneously capturing this major greenhouse gas and solving the shortage of sustainable energy. Efforts to demonstrate the photocatalytic reduction of CO₂ are reviewed herein. Although the photocatalytic results depended on the reaction conditions, such as the incident/absorbing light intensity from the sun or a simulated solar light source, the performance of different systems is compared. When the reactants included CO₂ and water, it was necessary to determine whether the products were derived from CO₂ and not from impurities that accumulated on/in the catalysts as a result of washing, calcination, or pretreatment in a moist environment. Isotope labeling of ¹³CO₂ was effective for this evaluation using Fourier-transform infrared (FTIR) spectroscopy and mass spectrometry (MS). Comparisons are limited to reports in which the reaction route was verified spectroscopically, the C source was traced isotopically, or sufficient kinetic analyses were performed to verify the photocatalytic events. TiO₂ photocatalytically produced methane at the rate of ~0.1 μmol h⁻¹ g_{cat}⁻¹. In aqueous solutions, formic acid, formaldehyde, and methanol were also produced. When TiO₂ was atomically dispersed in zeolites or ordered mesoporous SiO₂ and doped with Pt, Cu, N, I, CdSe, or PbS, the methane and CO formation rates were greater, reaching 1–10 μmol h⁻¹ g_{cat}⁻¹. As for semiconductors other than TiO₂, CdS, SiC, InNbO₄, HNb₃O₈, Bi₂WO₆, promoted NaNbO₃, and promoted Zn₂GeO₄ produced methane or methanol at rates of 1–10 μmol h⁻¹ g_{cat}⁻¹, and promoted A^{II}La₄Ti₄O₁₅ produced CO at a rate greater than 10 μmol h⁻¹ g_{cat}⁻¹, in addition to the historically known ZnO and GaP (formaldehyde and methanol formation). The photocatalytic reduction of CO₂ was also surveyed with hydrogen, because hydrogen can be obtained from water photosplitting by utilizing natural light. CO was formed at a rate of ~1 μmol h⁻¹ g_{cat}⁻¹ using TiO₂, ZrO₂, MgO, and Ga₂O₃, whereas both CO and methanol were formed at a rate of 0.1–1 μmol h⁻¹ g_{cat}⁻¹ using layered-double hydroxides consisting of Zn, Cu, Al,

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and Ga. When hydrogen is used, in addition to identifying the origin of the carbon, it is critical to confirm that the products are photocatalytically formed, not thermally produced via CO₂ hydrogenation. The feasibility of the strategy involving the recycling of a sacrificial electron donor and the direct supply of protons and electrons released from water oxidation catalysts to photocatalysts for the reduction of CO₂ to fuels has been demonstrated. However, based on the results obtained to date, it is clear that the practical use of the photocatalytic reduction of CO₂ as one possible solution for global warming and the world's energy problems requires the development of more efficient photocatalysts.

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1. Background

Owing to the limited amount of energy sources and the recent effects of fossil fuel use on the global environment, the paradigm of energy supply is changing from one based on the use of carbon-rich rocks, peat, and liquid found in the Earth to one based on renewable sources, such as energy crops, sunlight, and wind [1]. According to the Intergovernmental Panel on Climate Change (IPCC), oil (34.6%), coal (28.4%), gas (22.1%), and nuclear energy (2.0%) were major worldwide energy sources in 2008 (Fig. 1). The percentage of renewable energy was 12.9%; however, if the traditional simple burning of biomass (6.3%) is excluded, renewable energy accounted for only 6.6% of total consumption.

Carbon dioxide is one of the major greenhouse gases and is formed as a result of the consumption of fossil fuels [2]. In the CO₂ emission scenarios described for 2050, bioenergy (1.6×10^{20} Jy⁻¹), direct solar energy (3×10^{19} Jy⁻¹), and wind energy (2.5×10^{19} Jy⁻¹) are the top three renewable technologies that must be adopted in order to realize the ambitious target that calls for the decrease in the atmospheric CO₂ concentration to less than 440 ppm. Thus, renewable energy must be investigated intensively, because modern biomass, direct solar energy, and wind energy supply only 1.9×10^{19} , 0.5×10^{18} , and 1×10^{18} Jy⁻¹, respectively [1], and the application of renewable energy is increasing very slowly.

Several methods for reducing the CO₂ concentration in the atmosphere and preventing CO₂ emissions due to human activity have been investigated, such as investigating the sorption of CO₂ into new/functionalized materials; increasing the quantity of green carbon sinks (plants, phytoplankton, and algae containing chloroplasts); increasing the level of dissolved carbonate and its salts in sea water; or capturing CO₂ and transferring it to the bottom of the sea in a supercritical state [3].

It would be advantageous to capture CO₂ from the atmosphere or the exhaust of factories/power stations and convert it to fuel by using a sustainable source of energy such as sunlight. This option solves the problems of global warming and the sustainable energy shortage simultaneously [3–6]. It is an enormously difficult task

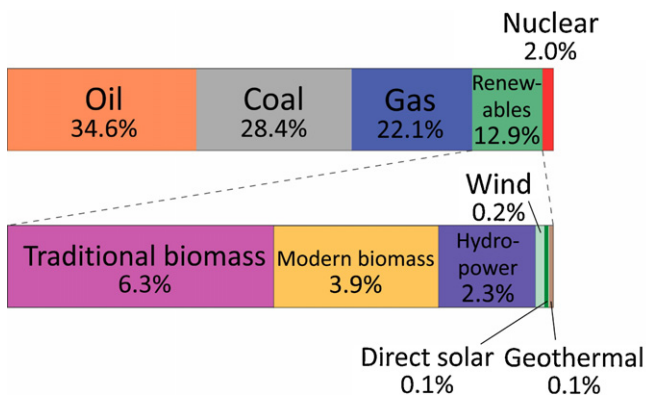
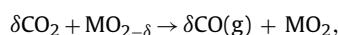
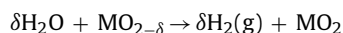


Fig. 1. 2008 distribution of world energy consumption by source [1].

to combine water splitting and carbon dioxide reduction [3,7,8]. Water oxidation and the subsequent reduction of CO₂ are required. This review mainly discusses the photocatalytic conversion of CO₂ to fuels (Sections 3–5) using semiconductors, but also presents a comparison of the related thermochemical conversion of CO₂ to fuels (Section 2) via the reduction–oxidation of metal oxides.

2. Thermochemical conversion of CO₂ to fuels

The energy from the sun that reaches the Earth in 1 h is 9200 times (4.3×10^{20} J h⁻¹) the energy consumed on the Earth in 1 h in 2001 (4.7×10^{16} J h⁻¹) [9]. In other words, all the energy consumed on the Earth in one year can be supplied from solar energy in only 1 h. To utilize the enormous energy provided by the sun, two-step thermochemical cycles to dissociate CO₂ and H₂O using metal oxide redox reactions have been proposed [10]. Nonstoichiometric oxides such as cerium oxide are partially reduced at higher temperatures (1873 K for cerium oxide), releasing O₂ under concentrated solar radiation, and then are oxidized again by reacting with CO₂ and H₂O at lower temperatures:



where M is Ce, Zn, or Fe, and the above stoichiometry represents an example for the case when M is Ce.

Compared to the redox systems consisting of Zn^{II}O–Zn⁰ and Fe^{II}Fe^{III}₂O₄–Fe^{II}O, cerium oxide is attracting attention because CeO₂ is partially reduced via the formation of an oxygen vacancy without significant reorganization of the crystal lattice, and therefore, it reversibly stores and releases lattice oxygen atoms. Furthermore, CeO₂ has a high melting point (2220 K), thermal stability, and is less susceptible to crystal-reordering phase transitions [11]. Above 1173 K under a solar flux with a density of 150 W cm⁻², the average evolution rate of O₂ was 0.049 mL min⁻¹ g_{cat}⁻¹ from cerium oxide, and the obtained partially reduced CeO_{2-δ} transformed CO₂ to CO at 1173 K at an average rate of 1.8 mL min⁻¹ g_{cat}⁻¹ and transformed H₂O to H₂ at 1173 K at an average rate of 0.95 mL min⁻¹ g_{cat}⁻¹ [10].

These thermochemical conversion rates are higher than the photocatalytic rates discussed below, but focusing lenses for sunlight and high-temperature reactors incur high initial investment costs.

3. Photon energy conversion of CO₂ to fuels with water

3.1. TiO₂ photocatalysts

The photon energy of sunlight can be converted to electric energy using solar cells [12] and to chemical energy using photocatalysts. The development of photocatalysts to convert solar energy to chemical energy is an indispensable option for storing energy and for mobile use, especially when using sustainable, cheaper

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