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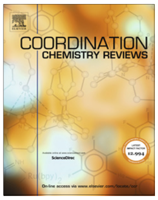

Review

Molecular catalysts of Co, Ni, Fe, and Mo for hydrogen generation in artificial photosynthetic systems

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A B S T R A C T

Driven by population and quality of living increases, the global consumption of energy is expected to dramatically increase over the course of the century. To avoid meeting this demand with fossil fuels, new carbon neutral energy sources must be implemented which are competitive in cost and performance with those currently in use. Hydrogen is a possible candidate to meet this need but carbon-free production of hydrogen needs to be developed. This chapter specifically examines the progress of homogeneous catalysts used in hydrogen production via artificial photosynthesis. Only those catalysts based on earth abundant metals, such as Co, Ni, Fe, and Mo are discussed as inexpensive mass production would require such materials, as opposed to expensive and rare metals, such as Pt, Pd and Rh. Electrocatalytic studies are also discussed as it pertains to the light driven systems and mechanistic insights.

Contents

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1. Introduction

The need for finding cleaner and sustainable fuels for mankind has been apparent for several decades, mainly as a result of a more thorough understanding of how CO_2 affects earth's climate and how particulate air pollution from fossil fuel combustion directly affects human health [1–4]. Additionally, geopolitical conflicts surrounding petroleum access and pricing are a somewhat regular and unsettling occurrence. However, driven by continued strong economic growth primarily in China and India, the world energy consumption is projected to increase by 56% by 2040 [1,2,5]. This new demand is also projected to be met largely by the burning of coal, resulting in an unprecedented 46% increase in atmospheric CO_2 as well as other pollutants. Furthermore, this dramatic increase in burning of fossil fuels will only hasten the exhaustion of natural reserves. Given these future projections, the time to identify and implement a high performing carbon neutral fuel is now.

Various strategies of renewable energy have already been actively pursued, such as biofuels, wind, hydroelectric, and solar. Each has their merits and should be a part of the future energy landscape but solar-based energy is the most viable solution for the long term [6,7]. It has often been said that more energy strikes the earth in one hour than mankind uses over an entire year [2]. Although harvesting this raw energy into useable energy is a significant challenge, doing so is the most dependable, long term solution for earth's energy [8]. Maximizing our ability to use the sun's energy will have long reaching benefits that could even go beyond use on earth. As humans look to send manned missions to Mars, solar energy is likely the only energy source that will be available.

Currently, photovoltaic (PV) cells are the main strategy for converting the sun's energy to electricity. There are three main drawbacks of PV cells: (1) reliance on sunlight to produce electricity, (2) relatively inefficient ability to harvest sunlight (~25%), and (3) a poor sunlight-energy demand overlap for grid power [2,6]. These drawbacks require a surplus electricity to be generated during the day and stored in batteries or capacitors, but given their maximum efficiencies, this would require excessive quantities of PV cells. A far more practical solution for storing solar energy is photochemical water splitting, generating hydrogen gas as a solar fuel. PV cells could, in fact, be used to supply electricity to a water electrolyzer as a way to create a "solar fuel," but the additive inefficiencies of both the PV cell and electrolyzer would require this model to be implemented on a large scale to produce the hydrogen required for modern vehicular travel. Another route to hydrogen via water splitting is artificial photosynthesis, a process where light is absorbed by a molecular compound, initiating a series of electron transfers involving catalysts that separately oxidize water to O_2 and reduce the liberated protons to H_2 [9–11]. This process has a distinct advantage over PV cells, as the sun's energy is stored in the chemical bonds of H_2 and as a chemical fuel, it can be made in excess and stored for use at any point [12]. The argument for artificial photosynthesis was first made over 40 years ago and significant progress has been made since then [4,13]. Due to the complexity of complete water splitting systems, the two sub-processes of water oxidation and proton reduction are typically studied separately. This chapter deals only with the progress toward catalytic aqueous light-driven proton reduction for hydrogen production using molecular species made up of Co, Ni, Fe, or Mo. Although Molybdenum has a long history in proton reduction, its application into light-driven molecular systems is very recent and its relative abundance makes it an exciting new area [14–21].

Proof of principle for artificial photosynthesis with molecular species was first reported in 1977 by Lehn and coworkers who showed that hydrogen could be produced from light irradiation using the combination of $[Ru(bpy)_3]^{2+}$ as photosensitizer, $Rh(bpy)_2Cl_3$ as electron mediator, triethanolamine (TEOA) as sacrificial electron donor, and K_2PtCl_6 as a precursor to Pt colloids, which serve as the catalyst for proton reduction [22]. Similar systems by Grätzel and Kagan closely followed still using $[Ru(bpy)_3]^{2+}$ as photosensitizer, methyl viologen (MX^{++}) as electron mediator, and TEOA and EDTA as electron donors, respectively [23,24]. Most notably, these studies more thoroughly investigated the mechanism of hydrogen formation through flash laser photolysis and both identified oxidative quenching of the ruthenium photosensitizer as the pathway for electron transfer.

The catalyst in many of these systems was colloidal Pt, which essentially served as a microelectrode for proton reduction [25–30], but cell-free hydrogenase was also examined, representing the beginning of biomimicry in this area [31–34]. It was noted that in some cases, hydrogen was produced in the absence of Pt [35], pointing to a Rh(III)-bipyridine complex (included to serve as an electron mediator) as the proton reduction catalyst [35]. Around the same time, homogeneous cobalt(II) macrocyclic complexes such as **C1** (Fig. 1), already known to catalytically reduce protons [36], were also employed in light-driven systems with $Ru(bpy)_3^{2+}$ (**P1a**) and either ascorbic acid (H_2A) or Eu(II) as electron donors [37]. These systems were significant because unlike those employing colloidal Pt, electrons could be transferred directly from photosensitizer to catalyst, eliminating the need for electron mediators. The mechanism for hydrogen formation was investigated in detail, leading to a likely mechanism in Fig. 1.

These initial reports of homogeneous hydrogen production, and in those that followed, shed light on how many paths can be taken to the formation of dihydrogen (Fig. 2) [14,38,39]. The process clearly begins with the photosensitizer (PS) absorbing light and entering a relatively long-lived excited state. Depending on the excited state oxidation/reduction potentials of photosensitizer,

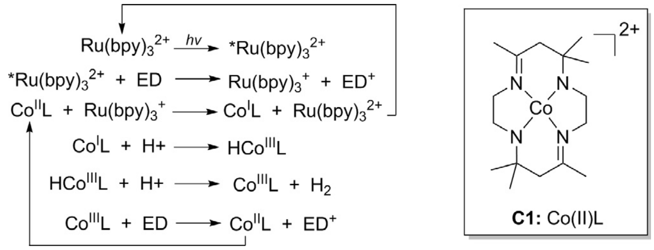

Fig. 1. Original mechanism proposed for first homogenous cobalt catalyst, shown on the right.

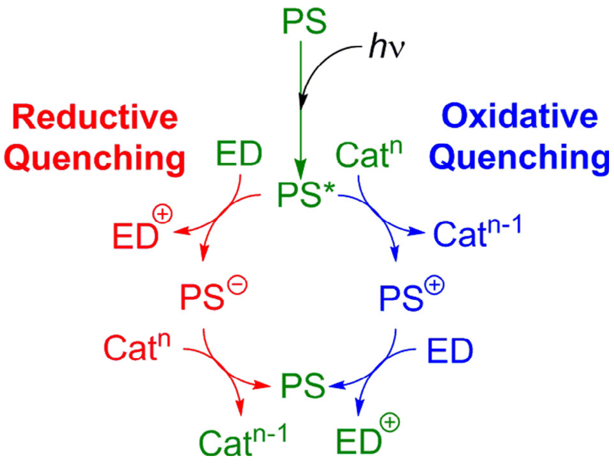

Fig. 2. General mechanisms of electron transfers leading to a reduced catalyst.

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