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PERSPECTIVE

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Renewable synthetic fuel: turning carbon dioxide back into fuel

Climate change has emerged as one of the major challenges worldwide. Since the First Industrial Revolution, the discovery and utilization of fossil energy has promoted the great prosperity and development of human society. Meanwhile, serious issues of environmental and climate change have arisen. In May 2021, CO_2 concentration in the atmosphere reached 419.13 ppm, observed by the National Oceanic and Atmospheric Administration (NOAA) of US, which arrives at the highest value in human history [1]. The CO_2-based greenhouse gas emissions lead to global warming, which causes a serious threat to the survival of human being as well as sustainable development of society. In September 2020, it was announced that China would scale up its nationally determined contributions and adopt more vigorous policies and activities to peak carbon dioxide emissions before 2030 and achieve carbon neutrality before 2060.

Carbon neutrality is a green revolution. Future energy for carbon neutrality urgently needs a series of disruptive and transformative energy technologies as strategic support. In view of the energy supply, the key to energy revolution lies in zero carbonization power and zero carbonization fuel [2]. Around the world, China ranks first in the scale of renewable energy development and utilization. According to the National Energy Administration of China, the total installed capacity of renewable energy power generation had reached 1.063 billion kilowatts by the end of 2021, accounting for 44.8% of the total installed capacity. Meanwhile, power generation from renewable energy has grown steadily, reaching 2.48 trillion kilowatt-hours, accounting for 29.8% of the total electricity consumption in China [3]. As predicted, China’s wind and photovoltaic (PV) power station installed capacity will reach 5 billion kilowatts in 2050. Due to the volatility, randomness, and intermittent characteristics of renewable energy, energy storage will become an indispensable technology combination for wind power and PV power generation, in order to improve the flexibility of power grid and overcome the problem of wind power and photovoltaic power rich abandonment. As an important type of chemical energy storage, using wind power, PV and other renewable energy sources to produce renewable fuels, including hydrogen, ammonia and synthetic fuels, will become a key aspect of future energy system for fuel zero carbonization and independence on fossil fuels, as shown in Fig. 1.

Using renewable electricity as a source of energy supply, renewable synthetic fuels, such as hydrocarbons, alcohols or ether fuels, can be produced by reduction of carbon dioxide, via thermal catalysis, electrocatalysis, etc. As an advanced energy storage technology, renewable synthetic fuel can achieve the effective circulation of carbon element. Compared with physical and electrochemical energy storage, it has the advantages of high energy density, easy storage and transportation, and long-term energy storage. Using the surplus zero-carbon electricity to produce renewable fuel will entirely change the utilization pathways of energy, from traditional online “source-grid-load” to brand-new offline “source-storage-load,” which will greatly improve the utilization rate of renewable energy and the level of on-site consumption. Overall, renewable synthetic fuel is a disruptive technology which will make transportation and industrial fuels independent on fossil energy, realize net zero carbon emission and provide new solutions for energy strategic transformation and carbon neutrality goals.

Research on renewable synthetic fuels must first refer to Olah, the Nobel Laureate in Chemistry, who proposed a far-sighted viewpoint of converting captured CO_2 into synthesize liquid renewable fuels, using primary energy

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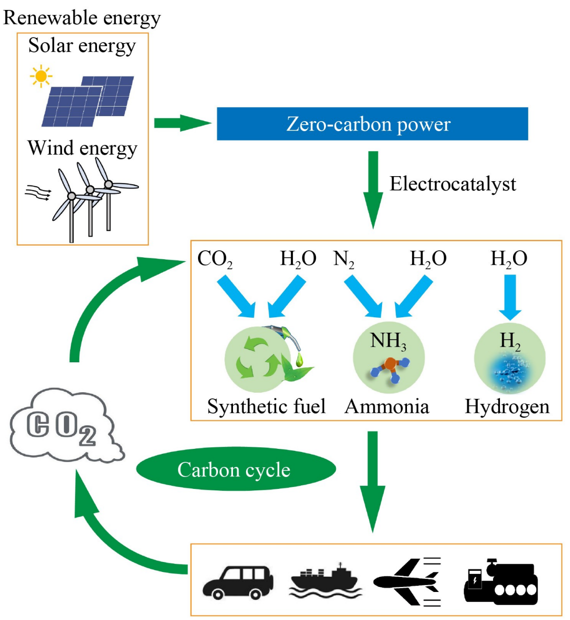

Fig. 1 Roadmap of renewable fuel production based on zero-carbon power.

from carbon-free sources [4,5]. In 2010, Jiang et al. highlighted three possible strategies turning CO_2 into fuels: sustainable synthetic methanol, syngas production derived from flue gases from coal-, gas- or oil-fired electric power stations, and photochemical production of synthetic fuels [6]. In 2018, Shih et al. proposed the roadmap to produce liquid sunshine methanol, combining solar energy with carbon dioxide and water. CO_2 released on using these green liquid fuels is recycled back into the environment, thus maintaining an ecologically balanced cycle [7]. Bushuyev et al. evaluated the current state of technology and the economics of electrocatalytic transformation of CO_2 into various chemical fuels, presenting economically compelling targets such as the current density, the overpotential, and the Faradaic efficiency (FE) [8]. In the past decade or so, the technology of converting CO_2 to synthetic fuels through renewable energy has attracted great attention in the world. In 2009, the US Department of Energy (DOE) established the Energy Frontier Research Center (EFRC) program, supporting basic researches on energy related electrocatalysis, photocatalysis, etc [9]. Forty-six centers were selected based on scientific peer review, which will provide a foundation for future advances in energy and environmental management [10]. Then, the Joint Center for Artificial Photosynthesis (JCAP) was established in 2010, which is the largest research program dedicated to the development of an artificial solar-fuels generation science and technology in the US [11]. In 2014, the EU-funded ENERGY-X project, aiming at building a strategic roadmap toward recycling of carbon-based energy using CO_2 as a medium, was launched to address the efficient conversion of solar and wind energy into chemical form [12]. The world's first demonstration of mega-watt scale syngas production by high-temperature co-electrolysis of water and CO_2 in an industrial environment was planned in EU HORIZON 2020 [13]. In Japan, the New Energy and Industrial Technology Development Organization (NEDO) allocated 4.5 billion Japanese yen for researches on technologies including co-electrolysis of water and CO_2 [14]. Hepburn et al. in the University of Oxford forecasted that up to 4.2 billion tons of CO_2 will be converted into synthetic fuels globally by 2050 [15]. Research reports from German Bosch shows that CO_2 emissions can be reduced by 2.8 billion tons (approximately 3 times the annual CO_2 emissions in Germany) by using synthetic fuels based on renewable energy in 2050 [16].

At present, thermal catalysis and electrocatalysis are promising technical routes for commercial production of renewable synthetic fuels. These technical routes share the features as follows: (1) zero-carbon electricity from renewable energy is required as energy input for the production process, since the CO_2 molecule is thermodynamically stable and the difference between standard molar enthalpy of formation is 283 kJ/mol from CO_2 to CO. (2) Activation of CO_2 molecule is needed due to the high energy barrier during the reaction process. Development of highly efficient catalysts to reduce the energy barrier of the catalytic reduction of CO_2 is the key step to improve the production process of renewable synthetic fuels. (3) External hydrogen sources are required to produce typical renewable synthetic fuels with C, H, and O elements. Typically, hydrogen is needed for thermal catalytic reduction and water is demanded as a proton source for electrocatalytic reduction of CO_2.

The thermal catalysis route is mainly based on zero-carbon electricity water electrolysis to generate hydrogen first, and then through CO_2 catalytic hydrogenation to produce methanol, methane, short-chain alkanes, aromatics, isomeric alkanes, and other products. Among these products, methanol and dimethyl ether are value-added products of CO_2 hydrogenation, as shown in Fig. 2. At present, there are two challenges in CO_2 hydrogenation to produce methanol. First, it is highly desirable to develop more efficient water electrolysis systems to produce hydrogen. Nowadays the electrolysis efficiency of commercial alkaline water electrolyzer is around 60%–80% [17]. It is expected that proton exchange membrane electrolysis cells and solid oxide electrolysis cells are effective solutions to achieve higher efficiency from electricity to green hydrogen. Secondly, in the viewpoint of thermodynamics, low temperature and high pressure are beneficial for CO_2 hydrogenation to methanol [18]. Low-cost, high-selectivity, and high-stability CO_2 hydrogenation catalysts are urgently to be developed, and novel reactors need to be designed. In the

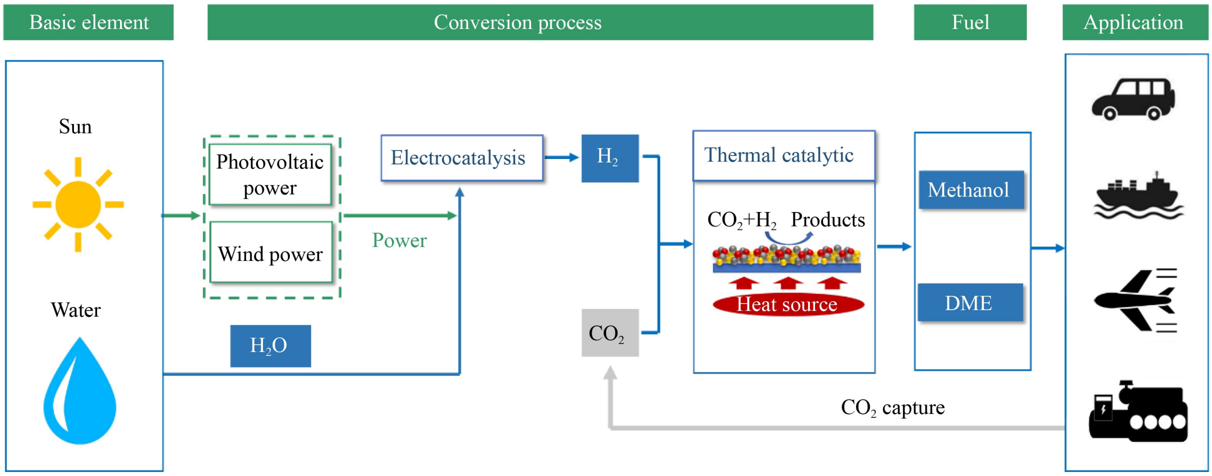

Fig. 2 Thermal catalysis route for preparing renewable synthetic fuels.

perspective of techno-economic analyses, the cost of green methanol produced by CO_2 hydrogenation is lower than traditional coal-based routes, if the cost of carbon emissions is taken into account [19]. Nowadays, renewable synthesis fuels produced via thermal catalysis has attracted increasing attention. For instance, Carbon Recycling International (CRI) built the world's first commercial methanol plant based on CO_2 recycling in Iceland. The production capacity of renewable methanol reached 4000 tons in 2014, with a combination of geothermal power generation, electrolysis of water to produce hydrogen (H_2), and synthesis of methanol by CO_2 hydrogenation [20]. In October 2020, the kiloton-level methanol production demonstration for liquid sunshine fuel synthesis was successfully launched in Lanzhou, China, by Dalian Institute of Chemical Physics, Chinese Academy of Sciences [21].

Electrocatalysis is defined as the technique that directly reduces CO_2 molecule to renewable synthetic fuels with catalysts and renewable electricity. It can be classified as low-temperature and high-temperature electrocatalysis, as demonstrated in Fig. 3. Low-temperature electrocatalytic reduction of CO_2 can obtain various products such as CO, formic acid, methanol, ethanol, and ethylene through the complex multiple proton-coupled electron transfer (PCET) process at room temperature and atmospheric pressure [22–24]. However, at present, it still faces many technical challenges, such as low current density, poor selectivity of products, low energy efficiency, low single-pass conversion of CO_2, and higher energy consumption of products separation [25]. To meet the demands of application at industrial level, rational design and optimization of electrocatalytic systems are necessary, including the development of high-selectivity and high-efficiency electrocatalysts, designing of gas diffusion electrode with high stability and high mass transfer rate, optimization of microenvironment in electrolyte, and engineering of electrolysis devices with low energy consumption and high reliability. For low-temperature electrocatalysis of CO_2, Sargent indicated that the economic benefit of producing value-added products would surpass existing petrochemical industry, when the selectivity of target product reached 90% and the energy conversion efficiency achieved 60% [8].

High-temperature CO_2 electrocatalysis refers to electrolysis using the high-temperature solid oxide electrolysis cell (SOEC) technology, typically operating at 600–850 °C [26,27]. High-temperature CO_2 electrocatalysis can be classified into direct electrolysis of CO_2 to CO and co-electrolysis of H_2O/CO_2 to H_2/CO syngas. Compared with direct electrolysis, the co-electrolysis process is able to generate controllable syngas ratios easily, which could be combined with the synthetic process to produce long-chain hydrocarbons, methanol, DME, and other fuels. Generally, high-temperature CO_2 electrolysis has the following advantages. The power demand is thermodynamically lower and the reaction rate is kinetically faster, which is able to improve overall energy efficiency and reduce costs [28]. The performance of SOEC units at the macro level is strongly associated with microscopic mechanisms, such as electrochemical reaction kinetics as well as heat and mass transfer mechanisms. Based on the fundamental rules of charge, heat, mass and transfer, it is of great necessity to conduct in-depth researches on key technologies such as electron collection on the interface, coating, connection, sealing, and assembly, which eventually fabricates a SOEC system with a higher current and lower degradation. Moreover, techno-economic factors for high-temperature CO_2 electrolysis have been analyzed by Ozden et al. With optimized costs of CO_2, electricity and electrolysis devices, the cost of CO produced via high-temperature electrolysis will be lower than that produced via traditional petrochemical routes [29,30].

The electrocatalytic route of producing renewable synthetic fuels has a huge market potential. In the future,

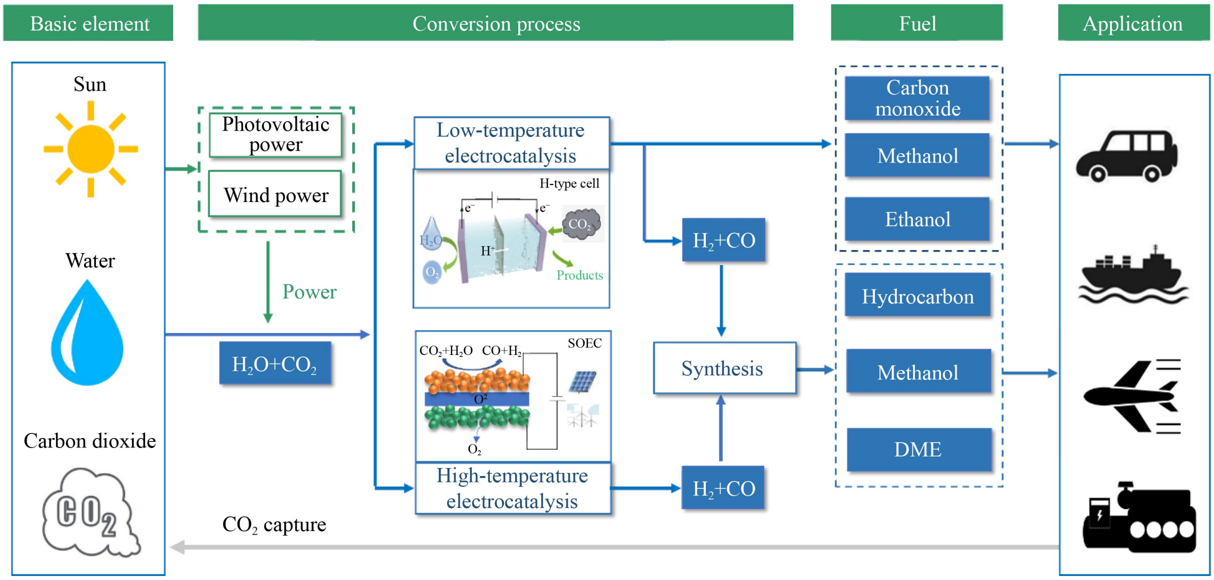

Fig. 3 Electrocatalysis route for preparing renewable synthetic fuels.

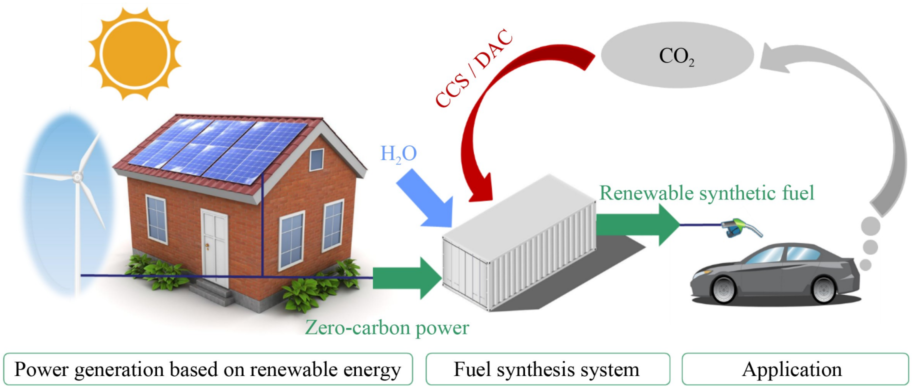

Fig. 4 Vision of future energy: Produce renewable synthetic fuels using the sun, water and CO_2.

the energy system will be established with new energy as the main body. Powered by zero-carbon electricity, distributed electrochemical units are possible to prepare renewable synthetic fuels from sunlight, water, and CO_2. CO_2 released on using these fuels can be recycled by carbon capture and storage (CCS) or direct air capture (DAC), which forms a carbon cycle, as depicted in Fig. 4. Future energy will go beyond fossil fuels, which will be a great energy revolution under the vision of carbon neutrality. In the past, human beings relied on the fossil fuels generated by sunshine hundreds of millions of years ago. In the future, daily sunshine will provide human beings with unlimited and inexhaustible heat, electricity, and renewable fuels.

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