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## Catalysis in sustainable energy resources: overview studies of hydrogen, methane, biomass and plastics

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The worldwide energy structure is gradually shifting from traditional fossil fuels to new energy sources. Through the rapid development of sustainable energy, it is possible to protect the environment, tackle climate change, and improve energy security, thereby achieving sustainable development. Catalysis is the basis of the modern chemical industry, and nowadays it plays an indispensable role in sustainable energy. In this review, some sustainable energy sources including methane, biomass, hydrogen, and plastics will be introduced as alternatives to fossil fuels with emphasis on the catalyst systems employed in the generation and conversion of these sustainable energy sources. We expect such a review paper to be an appetizer in the popular topic of catalysis for sustainable energy and can inspire future research to boost the development of this interdisciplinary field.

Keywords: Sustainable energy; Catalysis; Methane conversion; Biomass upgrading; Hydrogen energy; Plastics recycling.

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### 1 Introduction

There is a saying that the essence of energy utilization for humans is to boil water. The description is not very precise;

however, it does reveal that energy has the ability to do work. Water can be boiled from ambient temperature to ebullition with energy input. This is a simple example but enough to demonstrate the importance of energy. Energy exists in various forms, such as chemical, thermal, electrical, optical, and biological energy. These different forms of energy can be transformed into each other through physical and chemical processes, which is of utmost significance for modern civilization.

Due to the abundant supply and low price, fossil fuels have played an indispensable role in the history of human development. Nowadays, developments in drilling technology

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have made new reserves accessible, and these reserves require much more energy input to extract, thus reducing the net output energy of fossil fuels.<sup>1</sup> On the other hand, the utilization of fossil fuels causes a series of environmental problems, including pollution and climate change. By 2030, the annual production of coal, oil, and natural gas will be more than twice that can limit the global temperature rise to less than 1.5 °C if the current track keeps up.<sup>2</sup> At the same time, with the development of human society, a huge reduction in the demand for energy should not be an option. Therefore, it is urgent to use renewable or so-called sustainable energy to replace fossil energy. The falling cost and increasing efficiency of renewable energy indicate that the net energy of renewable energy is increasing. Brockway *et al.* have calculated the energy-return-on-investment ratios for fossil fuels and proposed that the net energy from fossil fuels may be far lower than previously believed and that renewable energy sources may already be competitive.<sup>1,3</sup>

Renewable energy includes solar energy, water energy, biomass energy, tidal energy, *etc.* These kinds of energy can be recycled, meaning that they are inexhaustible, in great contrast to traditional fossil fuels. Sustainable energy should be the key to future society. However, the situation of sustainable energy is not entirely optimistic. According to the UN tracking report, the share of renewable energy in total global energy consumption was just up to 19.1% in 2020, and one-third of it came from combustible resources like wood.<sup>4</sup> According to Renewables 2023 released by the International Energy Agency, the global annual renewable capacity increased by nearly 50% to nearly 5110 gigawatts (GW) in 2023, which is the fastest growth rate in the last 20 years.<sup>5</sup> Policy support, increased environmental awareness, and technological advancements are the main factors driving the growth of sustainable energy demand, which also means that the market demand for sustainable energy technologies is increasing. Human society has been constantly searching for new choices for sustainable energy and trying to improve the utilization efficiency.

Catalysis is a process in which a catalyst can alter, and typically speed up, the rate of a chemical reaction without

being consumed. Catalytic processes have been widely involved in energy conversion. Efficiency is always a major concern when discussing energy utilization and conversion, and catalysis plays a vital role in promoting efficiency. Although CO<sub>2</sub> conversion technologies play an extremely important role in sustainable energy, there are many nice review articles on this topic.<sup>6–11</sup> CO<sub>2</sub> conversion mainly focuses on how to convert emitted carbon dioxide into usable chemicals or fuels, which is indeed an important link in addressing climate change, but it is not a direct energy production technology. Besides, the core topics of the review are decided because they directly involve the production and use of renewable energy, while CO<sub>2</sub> conversion is more of an application in emission reduction and carbon management. For concise considerations, CO<sub>2</sub> conversion will not be included herein. In this review, we will introduce the catalytic systems with enormous application prospects in sustainable energy resources, from small molecules like hydrogen and methane to bulk molecules such as biomass and plastics, and present our perspectives on the potential of catalysis in sustainable energy utilization. We have selected some representative and influential cases in each technology field that can reflect the mainstream development direction and application scenarios of the technology. Hydrogen plays a key role in the transition to sustainable energy and methane is an important basic energy source which is currently irreplaceable. Catalytic conversion of biomass is a representative way of renewable energy utilization and plastic degradation to produce energy shows more possibilities for developing sustainable energy. Although these sustainable energy systems have been applied on a small scale in industrial production and daily life, they still have great room for improvement.

## 2 Catalysis in sustainable energy

Some sustainable energy sources, such as solar, hydro, and wind energy, usually do not require catalysts to participate in the production process. Currently, hydrogen generation, methane (CH<sub>4</sub>) conversion, biomass conversion and plastic degradation are the most representative catalytic reactions in the process of renewable energy production. The use of hydrogen energy can avoid the participation of carbon throughout the cycle, and the generation, storage, and transportation of hydrogen have many technical problems to be solved probably by means of catalysis. CH<sub>4</sub> is a widespread substance in nature, and it requires careful storage and transport against leakage because it is a strong greenhouse gas. In addition to extracting natural gas as fossil energy, it is easy to obtain CH<sub>4</sub> from biological fermentation and carbon dioxide (CO<sub>2</sub>) hydrogenation, providing sources of sustainable energy. Biomass is a well-known source of sustainable energy and the catalytic transformation of biomass requires efficient catalytic systems due to its structure complexity. Plastic, as a petrochemical product, has been widely used in many aspects of life, while plastics are difficult to be recycled and converted into fuel or valuable chemicals. Notably,



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there are many elegant review papers in related fields,<sup>12–16</sup> and herein an overview on catalysis in sustainable energy will be introduced from our own perspective.

## 2.1 Hydrogen

Hydrogen, one of the most promising forms of renewable energy, has the benefits of having no harmful by-products and no carbon emissions. Hydrogen may address the environmental problems on a worldwide scale and resolve the energy crisis. The problems with hydrogen production, transportation, storage, and utilization need to be considered to reach the full potential of hydrogen. The transportation and storage of hydrogen is a key issue. Currently, the dominant storage method for hydrogen is high-pressure hydrogen storage, which has low safety levels, demands pressure-resistant vessels, and requires significant compression work. Energy consumption, safety, and storage density (including mass and volume storage density) are major challenges for hydrogen storage technologies. There are some physical methods for hydrogen storage, but all have obvious shortcomings, such as high costs and energy consumption (cryogenic liquid hydrogen storage) and low volume storage capacity (adsorptive hydrogen storage).

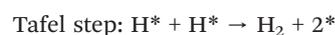
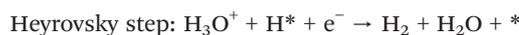
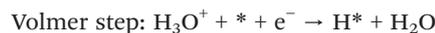
A suitable approach for hydrogen generation is a prerequisite for its application. On Earth, hydrogen is mainly stored in water, so finding a reasonable way to extract hydrogen from water should be the ideal choice. On the other hand, high storage capacity may be attained for hydrogen storage by employing certain molecules in reversible hydrogenation–dehydrogenation reactions. These molecules in the liquid phase, referred to as liquid hydrogen carriers (LHC), can be transported safely and conveniently at ambient temperature. In the next section, catalysis in hydrogen production from water splitting and hydrogen storage *via* LHC will be discussed.

### 2.1.1 Water splitting

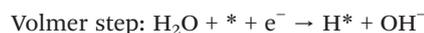
*Electrocatalysis for hydrogen evolution reaction.* Water splitting to produce high-purity hydrogen is an effective way

to convert renewable energy and store it without carbon involvement. Electrochemical water splitting is the most effective and direct method to produce hydrogen from water.<sup>17</sup> This reaction can be divided into two half-reactions, namely the oxygen evolution reaction (OER) at the anodic side and the hydrogen evolution reaction (HER) at the cathodic side (Fig. 1).<sup>18</sup> The HER is composed of multi-step elementary reactions.

In acidic medium:



In alkaline or neutral medium:



wherein \* represents the active site.<sup>19</sup>

The whole HER involves two steps of electron transfer and hydrogen desorption. During the actual reaction of HER, the adsorption and desorption of hydrogen atoms on the surface of a catalyst contribute to a pair of competitive reactions.<sup>20</sup> If the adsorption is too strong, it is easy to form H\*, but prevents H\* desorption to produce H<sub>2</sub>. In contrast, if the desorption is too strong, the reaction will be difficult to occur because of retention of few H\*. An ideal HER catalyst should show a balance between adsorption and desorption. From both theoretical and experimental perspectives, the Gibbs free energy of hydrogen adsorption ( $\Delta G_{\text{H}^*}$ ) is the key factor in describing the HER activity of a catalyst.<sup>21</sup> Besides, the kinetic barrier for water dissociation and OH binding energies may affect the catalytic activity in alkaline

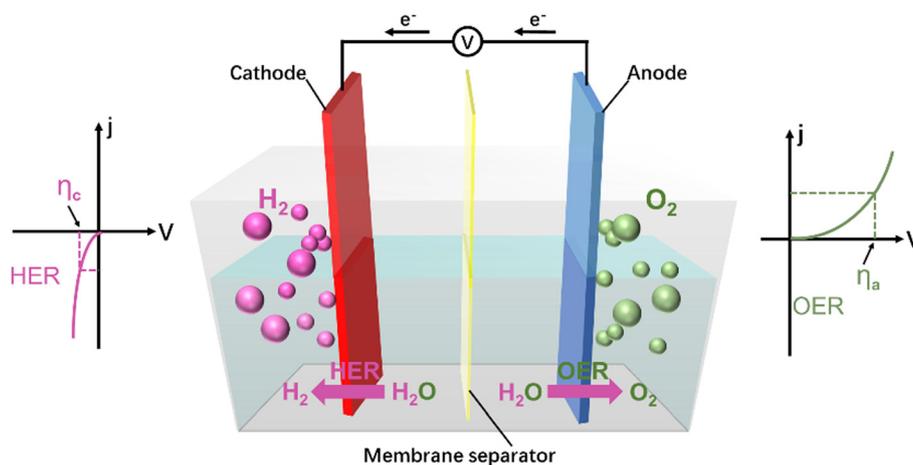


Fig. 1 HER and OER of electrocatalytic water splitting.<sup>18</sup> Modified with permission from ref. 18. Copyright (2020) ACS Publications.



environments.<sup>22</sup> Thus, tuning electrocatalysts to get a moderate  $\Delta G_{H^*}$  is crucial for exploring new catalysts. With the help of density functional theory (DFT), the binding energy (and the Gibbs free energy) of HER intermediates can be calculated according to the geometric and electronic structures. That is, DFT is a unique and effective tool for discovering new electrocatalysts for the HER, which should be verified by comparing the overpotential, Tafel slope, electrochemical impedance, stability, turnover frequency, faradaic efficiency, hydrogen bonding energy,  $\Delta G_{H^*}$ , etc. with reference samples.

The HER requires suitable catalysts to minimize the overpotentials, while the most effective electrocatalysts are noble metal catalysts. Platinum-group metal (PGM)-based catalysts such as Pt/C are recognized as the most efficient catalysts for the HER due to their optimum hydrogen binding energy and  $\Delta G_{H^*}$ .<sup>18</sup> Other noble metal-based catalysts like palladium also show impressive performance. However, it is frustrating that these noble metals are all in low abundance, corresponding to their high costs when used in industrial production. Therefore, the development of inexpensive catalysts, for example, non-precious metal and even non-metal electrocatalysts, is of great significance.<sup>23</sup> After years of attempts, the catalytic performance of some catalysts can be close to that of precious metal-based catalysts, while problems such as complex synthesis conditions and poor stability still exist.<sup>18</sup>

Recently, a large amount of work has focused on single-atom catalysts (SACs) to achieve maximized catalytic activity.<sup>24</sup> A major drawback of SACs is the lack of structural complexity, making them unsuitable for complex reactions. Nanocarbon materials such as graphene and carbon nanotubes have been applied as substrates in the synthesis of HER electrocatalysts (supported metal-based nanoparticles) with remarkable progress.<sup>25</sup> The size of nanoparticles can be reduced to several nanometers. Compared with nonporous catalysts, catalysts with porous structures have stronger constraints and may show higher catalytic activity. MOFs can be used as precursors/templates for the synthesis of porous carbons, which are widely adopted to obtain carbon-based materials with various morphologies and compositions.<sup>26</sup> Porous organic polymers are also ideal porous structures that can incorporate catalytically active sites into their frameworks or act as sacrificial precursors to synthesize porous catalysts with highly dispersed catalytically active sites.<sup>18</sup>

The HER provides a green and efficient pathway for the mass production of hydrogen and has great potential for industrial applications. However, during the reaction process, a complex structural reconstruction might occur on the catalyst surface, which will largely alter the chemical structure and environment of the active center, making it difficult to elucidate the underlying catalytic mechanism. In this context, the development of advanced *in situ* characterization techniques is needed to reveal the structural evolution of the active center and to guide the rational design of catalysts.<sup>18</sup>

### Photocatalysis for hydrogen evolution reaction.

Photocatalysis can convert light energy into chemical energy that is easier to store and use (Fig. 2).<sup>27,28</sup> Fujishima and Honda first reported that water splitting could occur on the TiO<sub>2</sub> surface in 1972.<sup>29</sup> For a very long time, solar-to-hydrogen (STH) energy conversion of photocatalytic water splitting reaches only around 1%, while the system design is much more amenable to scale-up. Domen *et al.* proved that photocatalytic water splitting could be expanded to a 100 m<sup>2</sup> scale without efficiency degradation.<sup>30</sup> Nevertheless, STH needs to reach 5–10% to achieve economically viable hydrogen production.<sup>31</sup> The stability of the catalyst can now be achieved for several months but still needs further optimization. Materials such as metal oxides, metal sulfides, MOFs, and covalent organic frameworks have all been applied in photocatalytic hydrogen production.<sup>32</sup> The light absorption efficiency of the catalyst can be effectively improved by adjusting the band structure of the semiconductor. Further development of new catalyst systems is still on the way.

**2.1.2 Liquid hydrogen carriers.** From a historical perspective, the idea of using LHC systems for hydrogen storage is not new, and the first research can be traced back to the 1980s.<sup>33</sup> Hydrogen storage with LHC can be divided into two stages, *i.e.*, i) hydrogen-lean molecules that can undergo the catalytic hydrogenation process to form molecules rich in elemental hydrogen and ii) hydrogen-rich molecules that can undergo dehydrogenation to close the cycle (Table 1).

The hydrogenation reaction of organic molecules is thermodynamically favorable, which allows for high conversion and selectivity. On the other hand, the dehydrogenation reaction is highly endothermic and thermodynamically unfavorable. Moreover, high-temperature sintering and coking can deactivate dehydrogenation catalysts. Consequently, a primary obstacle to establishing hydrogen storage using LHC is developing highly active and low-cost dehydrogenation catalysts. Fortunately, the difficult dehydrogenation step can be replaced by facile hydrolysis, also called as reforming. In this section, some representative examples of LHC catalysis will be discussed.

**Aromatics/cycloalkanes.** When the idea of LHC was first proposed, most research was concentrated on the hydrogen storage cycles of hydrocarbons based on benzene-based aromatics such as toluene/methylcyclohexane (MCH) and benzene/cyclohexane. In addition to these two traditional systems, more hydrogen storage pairs such as dibenzyltoluene (H0-DBT)/perhydro-dibenzyl toluene (H18-DBT) and naphthalene/hydrides of naphthalene (including tetralin and decalin) have been explored. In 2003, Air Products and Chemicals took the lead in using carbazole for hydrogen storage. Employing *N*-ethylcarbazole (NEC)/dodecahydro-*N*-ethylcarbazole (DNEC) for reversible hydrogen storage appears to be more promising as the reaction conditions are relatively mild.<sup>34</sup>



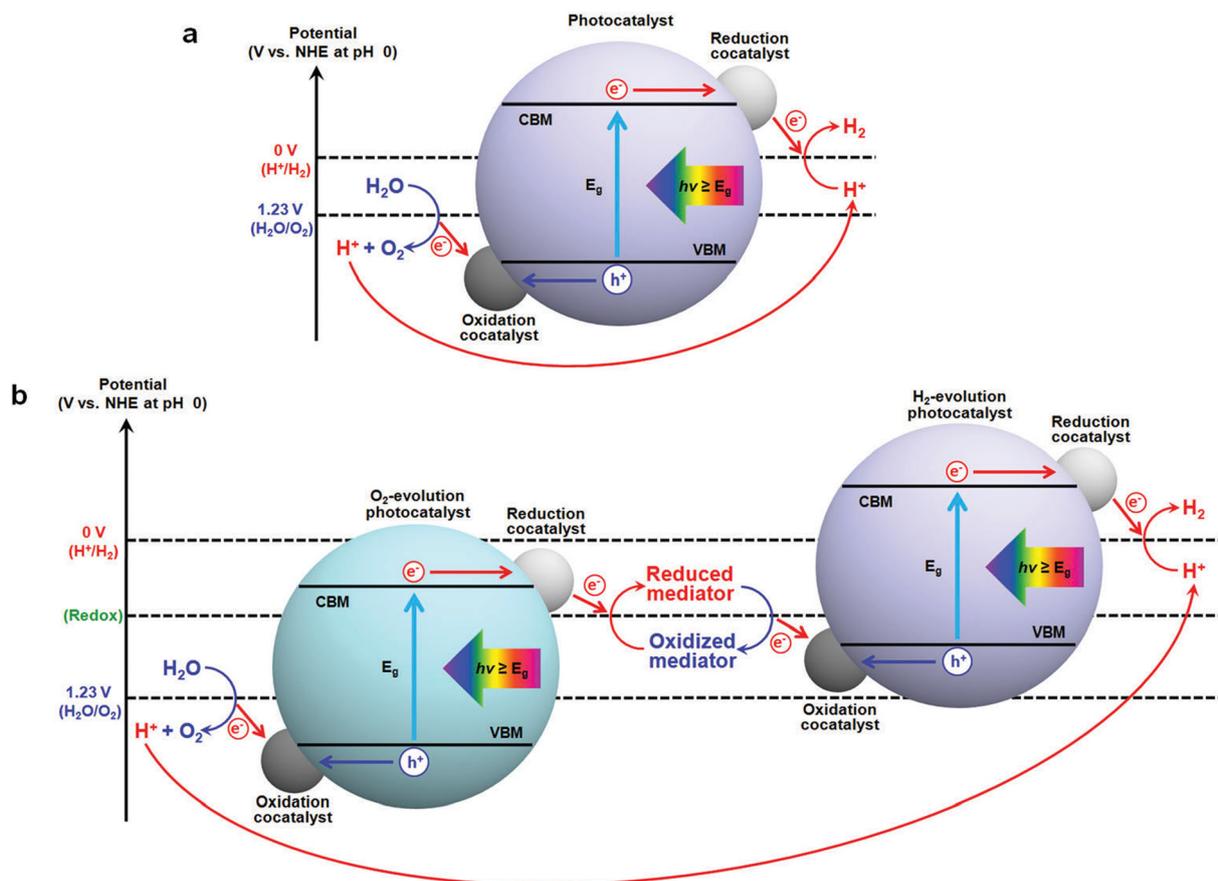


Fig. 2 Schematic of one-step excitation (a) and Z-scheme overall water splitting (b).<sup>27</sup> Modified with permission from ref. 28. Copyright (2019) ACS Publications.

Table 1 Properties of compounds for LHC

Hydrogen carrier	Dehydrogenated carrier	Volumetric density (g L <sup>-1</sup> )	Mass density (wt%)	Dehydrogenation enthalpy (kJ mol <sup>-1</sup> H <sub>2</sub> )
Cyclohexane (C <sub>6</sub> H <sub>12</sub> )	Benzene (C <sub>6</sub> H <sub>6</sub> )	56.3	7.1	68.6
Methylcyclohexane (C <sub>7</sub> H <sub>14</sub> )	Toluene (C <sub>7</sub> H <sub>8</sub> )	47.1	6.1	68.3
Dodecahydro- <i>N</i> -ethylcarbazole (C <sub>14</sub> H <sub>25</sub> N)	<i>N</i> -Ethylcarbazole (C <sub>14</sub> H <sub>13</sub> N)	—	5.8	50.6
Methanol (CH <sub>3</sub> OH)	Carbon dioxide (CO <sub>2</sub> )	99.8	12.6	16.5
Ammonia (NH <sub>3</sub> )	Dinitrogen (N <sub>2</sub> )	108	17.7	30.6
Hydrous hydrazine (N <sub>2</sub> H <sub>4</sub> ·H <sub>2</sub> O)	Dinitrogen (N <sub>2</sub> )	82.6	8.0	-25.3
Ammonia borane (NH <sub>3</sub> BH <sub>3</sub> )	Ammonium metaborate (NH <sub>4</sub> BO <sub>2</sub> )	145	19.6	-52

The Gibbs free energy change of aromatic hydrogenation is negative, frequently with a significant value. The hydrogenation reaction is therefore thermodynamically favorable, while the dehydrogenation reaction is endothermic, requiring high temperatures and low pressures and being constrained by reaction equilibrium. Dehydrogenation catalysts are prone to coking and deactivation under high-temperature conditions, and the selected catalyst should avoid potential side reactions involved in the process as much as possible, such as hydrogenolysis.

Pt plays an undeniable role in the dehydrogenation of cycloalkanes and their derivatives. However, the low natural abundance and high cost of Pt prevent it from being used

massively in industry. Optimizing atomic efficiency and reducing industrial costs can be achieved by decreasing Pt particle size. For example, Chen *et al.* used a modified ascorbic acid-assisted reduction technique to prepare a single-site Pt<sub>1</sub>/CeO<sub>2</sub> catalyst (Fig. 3),<sup>35</sup> showing unique performance in the reversible dehydrogenation and hydrogenation of large molecules like cyclohexane and methylcyclohexane.

For carbazole molecules, especially dodecahydro-*N*-ethylcarbazole (DNEC), Pd catalysts have been extensively investigated since the first report by Smith *et al.*<sup>36</sup> Most recently, Ge *et al.* developed a two-dimensional magnesium hydroxide nanosheet that supports Pd clusters for the



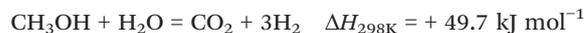
dehydrogenation of DNEC, offering 100% DNEC conversion and 5.72 wt% hydrogen release with only 0.5 wt% Pd loading at 180 °C.<sup>37</sup>

Although Pt and Pd perform well in dehydrogenation reactions, their scarcity and high cost limit the industrial application in LHC systems. Therefore, the development of non-noble metal-based catalysts has been attempted, and Ni (ref. 38) and Zn (ref. 39) are two examples that show decent catalytic activity. Compared to monometallic catalysts, bimetallic catalysts are crucial in promoting the performance in various reactions such as the dehydrogenation of cyclohexane.

The dehydrogenation reaction can also be accomplished by photocatalysis. Li *et al.* reported Pt/black TiO<sub>2</sub> photocatalysts for non-oxidative dehydrogenation of alkanes at room temperature.<sup>40</sup> This catalyst reached a turnover number of over 100 000 without deactivation after 80 reaction cycles in cyclohexane dehydrogenation.

**Carbon dioxide/methanol.** CO<sub>2</sub> emissions rise with the use of fossil fuels. Reducing the excessive concentration of CO<sub>2</sub> in the atmosphere is possible with the help of carbon capture and utilization. In this context, the reduction of CO<sub>2</sub> by H<sub>2</sub> to produce CH<sub>3</sub>OH is a feasible method to reduce CO<sub>2</sub>

concentration in the atmosphere. Methanol has great potential as LHC. It can store 12.6 wt% H<sub>2</sub> in each molecule, which is significantly higher than cyclohexane and some other LHC molecules (Table 1). As a stable liquid at room temperature, it is easy to transport. As shown in the following equation, CH<sub>3</sub>OH can produce H<sub>2</sub> through the methanol steam reforming (MSR) reaction.



Due to the absence of C–C bonds in methanol molecules, the MSR reaction can be achieved at relatively low temperatures of 150–350 °C, in comparison with other alcohols and hydrocarbons. The main drawback of MSR is the by-product from methanol decomposition and the reverse water-gas shift reaction, CO, which can poison Pt-based catalysts in fuel cells. Moreover, CO and another by-product CH<sub>4</sub> can reduce the purity of H<sub>2</sub>, which poses additional issues for H<sub>2</sub> purification. Therefore, for the MSR reaction, developing appropriate catalysts with perfect selectivity is the key research target.

At present, the main process of MSR is still the thermocatalytic approach. Various catalysts, including Cu, Pt,

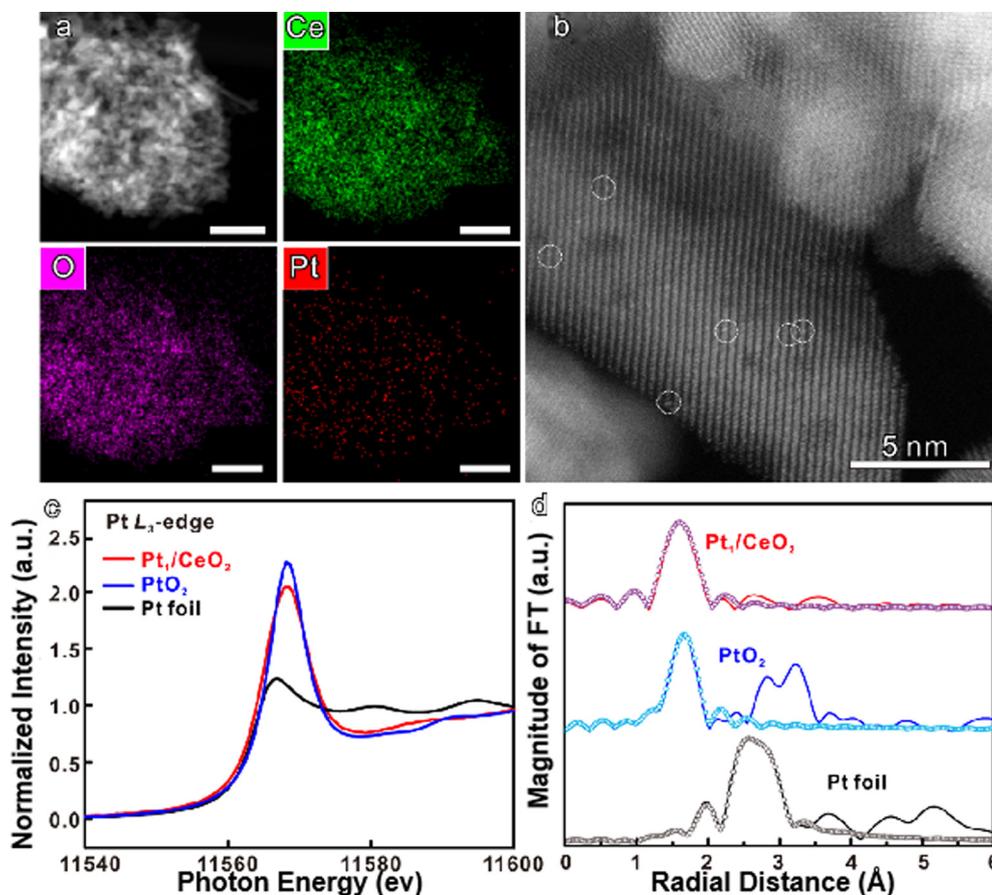


Fig. 3 (a) HAADF-STEM images and elemental mapping images of the Pt<sub>1</sub>/CeO<sub>2</sub> catalyst; (b) Cs-corrected HAADF-STEM images of the Pt<sub>1</sub>/CeO<sub>2</sub> catalyst; (c) Pt L<sub>3</sub>-edge XANES spectra of Pt<sub>1</sub>/CeO<sub>2</sub>, PtO<sub>2</sub>, and Pt foil; (d) k<sup>3</sup>-weighted Fourier transform EXAFS spectra (L<sub>3</sub>-edge) of Pt<sub>1</sub>/CeO<sub>2</sub>, PtO<sub>2</sub>, and Pt foil.<sup>35</sup> Modified with permission from ref. 35 Copyright (2022) Springer Nature.



Pd, and metal oxide-based catalysts, have been explored for potential applications in MSR. Due to its low price and excellent activity in MSR, Cu has been extensively studied and often used with ZnO as a modifier to construct efficient catalyst systems. The synergistic effect between Cu and ZnO has been widely studied, and Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> is commercially used as a benchmark catalyst. Recently, Li *et al.* studied the effect of the activation process on the catalytic activity of the commercial Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst,<sup>41</sup> and concluded that the catalyst reduced by H<sub>2</sub> followed by a pretreatment under H<sub>2</sub>/H<sub>2</sub>O/CH<sub>3</sub>OH/N<sub>2</sub> exhibited the best activity and stability.

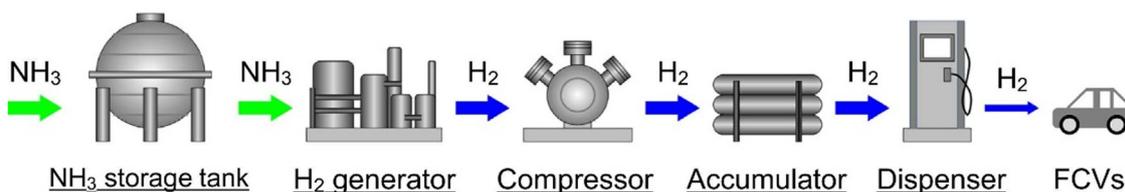
In addition to thermocatalysis, other approaches like biocatalysis, photocatalysis, and electrochemical catalysis have shown some potential in MSR. In 2015, Heim *et al.* constructed the first effective system for CH<sub>3</sub>OH reforming at room temperature in an aqueous medium *via* the combination of enzyme catalysis and metal catalysis.<sup>42</sup> Photocatalytic CH<sub>3</sub>OH reforming also demonstrates its potential. Recently, Ćwieka *et al.* achieved the efficient photo reforming of CH<sub>3</sub>OH using a simple and inexpensive Cu/TiO<sub>2</sub> photocatalyst.<sup>43</sup> Electrochemical methanol dehydrogenation can provide electricity directly through fuel cells.<sup>44</sup> Direct fuel cells feed methanol on the fuel cell anode to make protons and carbon dioxide, which can simply convert fuel into electrical energy. The most serious and urgent problem of this technology is methanol crossover due to the high solubility of methanol in the electrolyte.<sup>45</sup> Therefore,

methanol aqueous solution is generally added as fuel in batteries. In addition, methanol permeation can be reduced by improving the permeable membrane.<sup>46</sup> At present, applying MSR directly to fuel cells typically has a much shorter lifespan than proton fuel cells, which greatly limits its industrial applications.<sup>44</sup>

**Dinitrogen/ammonia.** Ammonia and its derivatives, including hydrazine hydrate and ammonia borane, can also be used as LHC (Fig. 4).<sup>47</sup> As ammonia production is a mature industry process, NH<sub>3</sub> decomposition and H<sub>2</sub> separation are the two main challenges. Among all transition metals, Ru is the most active for ammonia decomposition due to the suitable strength of the Ru–H bond.<sup>47,48</sup> Pressure swing adsorption appears to be suitable for H<sub>2</sub> recovery from the NH<sub>3</sub>/N<sub>2</sub>/H<sub>2</sub> mixture.<sup>49</sup>

Ammonia borane is a good candidate for LHC due to its high hydrogen content of 19.6 wt%.<sup>50</sup> Ammonia borane can release H<sub>2</sub> in the presence of water and methanol with the help of catalysts, which will not release any gaseous by-products at low temperatures. It is noteworthy that the bimetallic catalysts can effectively improve the catalytic activity because of the synergistic effects.<sup>51</sup> Hydrous hydrazine (N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O) also has a high hydrogen content of 8.0 wt%.<sup>52</sup> The complete decomposition of N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O is an ideal reaction to produce H<sub>2</sub>, while the incomplete decomposition will produce NH<sub>3</sub> and poison catalysts.

#### (a) Process of on-site NH<sub>3</sub>-decomposition H<sub>2</sub> fueling station



#### (b) Components of H<sub>2</sub> generator and gas flow

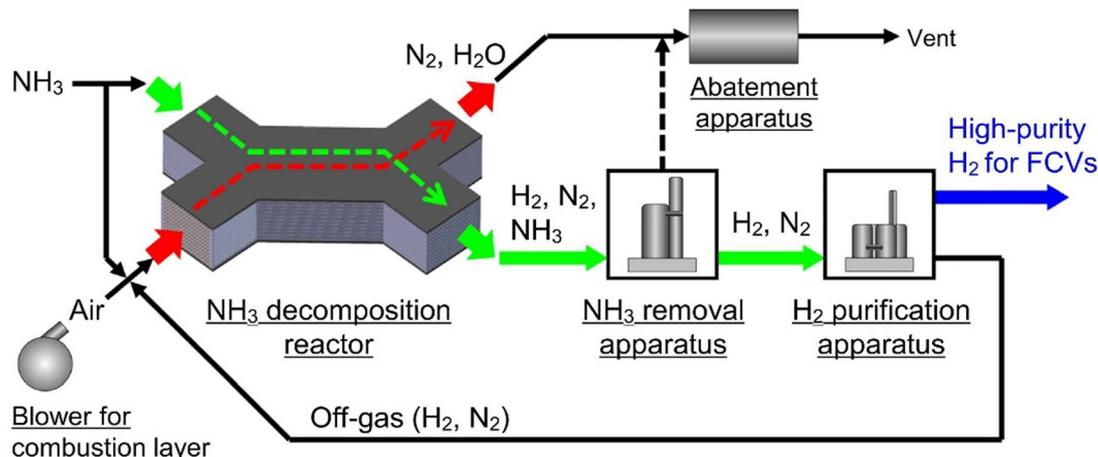


Fig. 4 Scheme of the NH<sub>3</sub>-decomposition fueling station. Modified with permission from ref. 47. Copyright (2023) Elsevier.



*Electrochemical liquid organic hydrogen carriers (EC-LOHC).* As electrochemical (EC)-LOHC (de)hydrogenation technology can function at relatively low temperatures and pressures, it can address issues with existing thermochemical LOHC systems.<sup>53,54</sup> EC-LOHC can directly use LOHC as fuel in fuel cells, similar to direct alcohol fuel cells, using liquid organic fuels such as methanol, ethanol, and formic acid at the anode. These alcohol fuel cells are usually nonrenewable and emit carbon dioxide. In contrast, LOHC generates energy and produces dehydrogenation products during the dehydrogenation process (electro-oxidation), which can be further recycled after hydrogenation (electro-reduction).<sup>55</sup> This technology can avoid carbon dioxide emissions during use and is more in line with the current concept of carbon neutrality. The high structural stability in electro-oxidation/reduction is an important criterion for whether organic compounds can be used as hydrogen carriers.<sup>55</sup> The carriers generally undergo decomposition (such as dehydroascorbic acid decomposition at pH > 8) and polymerization (such as electro polymerization of catechol under at pH ≥ 10) under voltage.<sup>56,57</sup> In addition, electro oxidation must be carried out at a potential lower than the oxygen reduction reaction (ORR) to avoid irreversible oxidation.<sup>55</sup>

At present, isopropanol (IPA)/acetone is considered the most promising candidate for EC-LOHC first reported by Wang *et al.*<sup>58</sup> Although alcohols have faster kinetics in alkaline media than in acidic media, their performance deteriorates rapidly.<sup>59</sup> Besides, the produced acetone will poison the metal catalyst, leading to catalyst deactivation.<sup>60,61</sup> Therefore, it is very urgent to develop new catalysts. Phenolic compounds (especially *o*-quinone/catechol) and organic acids (especially L-ascorbic acid/dehydroascorbic acid) have also been applied in the EC-LOHC system.<sup>62,63</sup>

## 2.2 Methane catalytic conversion

Methane, a well-known abundant fossil source or possible sustainable energy source, has been widely used in industry and daily life. The significant advantage of CH<sub>4</sub> is that it has the highest mass heat of about 56 kJ g<sup>-1</sup> as compared to other hydrocarbons.<sup>64</sup> The reserves of CH<sub>4</sub> are quite impressive. It is predicted that CH<sub>4</sub> hydrate and shale gas reserves far exceed the total of other fossil fuels. CH<sub>4</sub> has the advantages of easy production, low cost, and relatively small pollution, while the feasible storage and transportation of CH<sub>4</sub> remain big challenges. CH<sub>4</sub> is a strong greenhouse gas that has a greenhouse effect that is 21 times greater than CO<sub>2</sub>. The main transportation and storage method is liquefied natural gas at a low temperature of <111 K, and under such circumstances, container breakage and the resulting CH<sub>4</sub> leakage are inevitable, which is quite harmful to the environment.<sup>65</sup> Due to the lack of rational conversion paths of CH<sub>4</sub> into other cost-effective petrochemical products, the sustainable application of CH<sub>4</sub> is significantly inhibited.

Methane conversion can be achieved through direct and indirect routes. The indirect conversion routes generally refer

to converting CH<sub>4</sub> into syngas through various pathways and converting syngas into more manageable methanol or liquid hydrocarbons. Typically, syngas can be obtained through the following routes: dry reforming of CH<sub>4</sub> (DRM), steam reforming of CH<sub>4</sub> (SRM), and partial oxidation of CH<sub>4</sub> (POM). Although the total conversion of CH<sub>4</sub> is relatively high in the indirect CH<sub>4</sub> conversion routes, the production of syngas intermediate is a high-cost and high-temperature process, which limits its application. The direct conversion routes mainly include oxidative and non-oxidative coupling, pyrolysis, aromatization, and partial oxidation. The original intention of developing direct conversion routes is to bypass complex intermediate steps to reduce costs. However, due to the high reaction temperature employed, the low CH<sub>4</sub> conversion, and the complex product separation process, the direct conversion routes still cannot meet the original intention.

The difficulty of CH<sub>4</sub> conversion lies essentially in its unique structure. Methane has a symmetrical tetrahedral structure with a high C–H bond energy of 438.8 kJ mol<sup>-1</sup>, meaning that the activation of such C–H bonds is quite difficult. Efficient catalytic systems might be the key to overcoming this challenge. The direct conversion routes should be more cost-effective and show greater potential in future applications than the indirect routes, considering the simpler processes involved in the former ones. In this section, we will focus on the direct conversion of CH<sub>4</sub>. Thereinto, the catalytic oxidative coupling and partial oxidation of CH<sub>4</sub> are the mainstream application directions.

**2.2.1 Oxidative coupling of methane.** Oxidative coupling of methane (OCM) is a promising strategy to produce C<sub>2</sub> hydrocarbons, as shown in the following reaction equations [eqn (1) and (2)].<sup>64</sup>



In the past decade, OCM with dioxygen (O<sub>2</sub>-OCM) has reignited global interest. For this reaction, one of the biggest challenges is the low selectivity to and yield of C<sub>2+</sub> hydrocarbons.<sup>66</sup> The main reason is the formation of CO<sub>x</sub> byproducts, which are produced from over-oxidation at high reaction temperatures.<sup>67</sup> It has been estimated that the yield of C<sub>2</sub> needs to reach 30% to meet industrial criteria, while few catalytic systems can achieve this goal.<sup>68</sup> In early research, Mn<sub>2</sub>O<sub>3</sub>-Na<sub>2</sub>WO<sub>4</sub>/SiO<sub>2</sub> was developed as a benchmark catalyst due to the simultaneously obtained high C<sub>2</sub> selectivity (60–80%), CH<sub>4</sub> conversion (20–30%), and good stability (hundreds of hours) at high temperatures of >800 °C.<sup>65</sup> Since its discovery, this catalyst has been extensively studied in preparation, modification, catalytic mechanism, and modeling. Using Ti-MWW zeolite as a support and TiO<sub>2</sub> as a dopant, Wang *et al.* reported a TiO<sub>2</sub>-doped Mn<sub>2</sub>O<sub>3</sub>-Na<sub>2</sub>WO<sub>4</sub>/SiO<sub>2</sub> catalyst achieving 26% CH<sub>4</sub> conversion and 76% C<sub>2</sub>-C<sub>3</sub> selectivity at 720 °C in the OCM reaction. The good performance is ascribed to the formation of MnTiO<sub>3</sub>.<sup>69</sup>

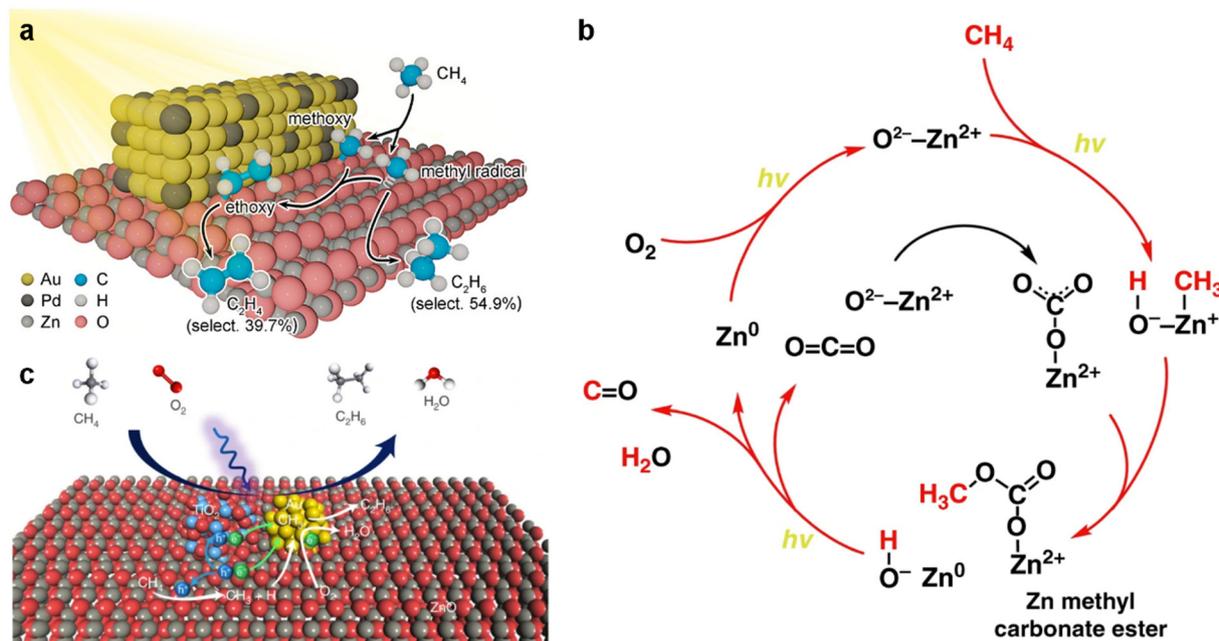


Furthermore, the ball mill method was employed in the preparation of the  $\text{Mn}_2\text{O}_3\text{-TiO}_2\text{-Na}_2\text{WO}_4/\text{SiO}_2$  catalyst that could be transformed *in situ* into  $\text{MnTiO}_3\text{-Na}_2\text{WO}_4/\text{SiO}_2$ , which achieved 22% conversion and 62% selectivity at a lower temperature of 650 °C. These findings might lead to the practical development of a low-temperature OCM process. Modifying  $\text{Na}_2\text{WO}_4/\text{SiO}_2$ -based catalysts for the OCM reaction at low temperatures has been continuously explored. For example, Zou *et al.* reported that methyl radicals generated by  $\text{La}_2\text{O}_3$  could selectively couple on the surface of 5%  $\text{Na}_2\text{WO}_4/\text{SiO}_2$ , offering a high  $\text{C}_2$  yield of 10.9% at 570 °C.<sup>70</sup>

In addition to the thermocatalytic manner, the photocatalytic OCM reaction has attracted much attention recently. Photocatalysis can activate the C–H bonds of  $\text{CH}_4$  even at room temperature. Moreover, the reaction does not require crossing extremely high energy barriers and has high selectivity.<sup>71</sup> However, uncontrolled overoxidation to  $\text{CO}_2$  and  $\text{CO}$  is more likely to occur. Preventing the overoxidation of  $\text{CH}_4$  is one of the key concerns in photocatalytic OCM reactions. Among the several semiconductors tested for photocatalytic OCM, two simple oxides, namely  $\text{TiO}_2$  and  $\text{ZnO}$ , appear to be candidate photocatalysts and show different characteristics.  $\text{TiO}_2$  is more active for  $\text{CH}_4$  conversion, while  $\text{ZnO}$  is more selective for  $\text{C}_2$  hydrocarbon production.  $\text{ZnO}$  possesses an abundance of  $\text{Zn}^+\text{-O}^-$  pairs as surface active sites (Fig. 5a and b).<sup>72,73</sup> Under light excitation,  $\text{O}^-$  sites have the ability to break the C–H bond of  $\text{CH}_4$  to produce methyl radicals, while  $\text{Zn}^+$  sites aid in anchoring the methyl radicals produced for subsequent reactions.<sup>74</sup> As for  $\text{TiO}_2$ , a large number of holes and excited electrons formed

on the catalyst surface subsequently encourage oxidative and reductive reactions, respectively.<sup>75</sup> It is therefore rational to design  $\text{ZnO}/\text{TiO}_2$  hybrids at the nanoscale for the photocatalytic OCM reaction. Song *et al.* reported that highly selective and efficient photo-oxidation of  $\text{CH}_4$  to ethane ( $\text{C}_2\text{H}_6$ ) could be achieved in a flow reactor utilizing an Au nanoparticle loaded  $\text{ZnO}/\text{TiO}_2$  hybrid (Fig. 5c).<sup>76</sup> A high  $\text{C}_2\text{H}_6$  production rate ( $>5000 \mu\text{mol g}^{-1} \text{h}^{-1}$ ) with high selectivity ( $>90\%$ ) was obtained on the optimized catalyst. The good activity and low overoxidation ability are ascribed to the heterojunction structure between  $\text{ZnO}$  and  $\text{TiO}_2$ . During the reaction, the photoelectrons generated from  $\text{ZnO}$  and  $\text{TiO}_2$  transfer to Au nanoparticles and reduce  $\text{O}_2$  to  $\text{O}_2^-$  radicals. At the same time, the holes on  $\text{ZnO}$ , which are generated from  $\text{TiO}_2$  and move to  $\text{ZnO}$  subsequently or generated on  $\text{ZnO}$  directly, abstract the H atom from  $\text{CH}_4$  and produce the  $\cdot\text{CH}_3$  species. The Au nanoparticles contribute to the desorption of methyl radicals from the catalyst surface to the gas phase, which subsequently combine with each other for  $\text{C}_2\text{H}_6$  production. The synergy effect between  $\text{ZnO}$  and  $\text{TiO}_2$  makes this catalyst show enhanced activity compared to  $\text{ZnO}$  and  $\text{TiO}_2$  alone.

**2.2.2 Partial oxidation of methane.** The direct oxidation of methane to methanol is attractive since methanol is a bulk and platform chemical widely used in industry. In current industry production, the conversion of methane to methanol is mainly achieved *via* the indirect route through the high-temperature reforming of  $\text{CH}_4$  followed by high-pressure methanol ( $\text{CH}_3\text{OH}$ ) synthesis from syngas. These processes are complex and require high energy consumption, which in



**Fig. 5** (a) Scheme of photocatalytic OCM reactions on Pd-modified  $\text{ZnO-Au}$ . Modified with permission from ref. 72. Copyright (2021) ACS Publications. (b) Scheme of reaction steps in methane photo-oxidation over  $\text{Zn-HPW}/\text{TiO}_2$ . Modified with permission from ref. 73. Copyright (2019) Springer Nature. (c) Scheme of photocatalytic OCM reactions on an Au nanoparticle (NP) loaded  $\text{ZnO}/\text{TiO}_2$  hybrid. Modified with permission from ref. 76. Copyright (2021) Springer Nature.



some ways limits the large-scale use of CH<sub>4</sub>, especially for CH<sub>4</sub> produced from decentralized locations. The chemical utilization of CH<sub>4</sub> might be revolutionized by the direct conversion route, which is commonly seen as a “holy grail” in the chemical utilization of CH<sub>4</sub> and catalysis. The difficulty of this route arises from both the selectivity control resulting from the much higher reactivity of CH<sub>3</sub>OH than CH<sub>4</sub> and the activation of CH<sub>4</sub> molecules with inert C–H bonds.

Recently, van Bokhoven *et al.* reviewed the latest progress of CH<sub>4</sub> partial oxidation in thermochemistry, photochemistry, electrochemistry, and non-thermal plasma.<sup>77</sup> It is pointed out that the use of thermal and thermocatalytic strategies to achieve CH<sub>4</sub> partial oxidation contributes to the largest portion of the published literature, mainly due to the precedents of conventional chemical processes and the availability of experimental techniques for these systems. Herein, only the most important and very recent examples will be introduced to avoid too much repetition. In 2023, Wang *et al.* reported the selective oxidation of CH<sub>4</sub> to CH<sub>3</sub>OH in aqueous medium with the presence of CO using gold nanoparticles dispersed on mordenite as a catalyst.<sup>78</sup> It was uncommon to witness the reaction, which is challenging to carry out without the involvement of CO. Both CO<sub>2</sub> and oxygenated products are formed when CO is introduced. According to the experiment results, the active oxygen species produced by CO–O<sub>2</sub> is similar to that produced by H<sub>2</sub>O<sub>2</sub> over the Au/H-MOR catalyst. At 150 °C, methanol productivity reaches 1300 μmol g<sub>cat</sub><sup>-1</sup> h<sup>-1</sup> with 75% selectivity, higher than

most catalysts under comparable conditions. Reducing the reaction temperature for this reaction is one of the goals being pursued, while it remains a huge challenge due to the intrinsic chemical inertness of CH<sub>4</sub>. So far, CH<sub>4</sub> monooxygenase (MMO) is the only known natural catalyst that can effectively drive the conversion of CH<sub>4</sub> and O<sub>2</sub> at room temperature.<sup>79</sup> Apart from enzyme catalysis, conducting in-depth research in heterogeneous catalysis considering economy is important and necessary. Hutchings *et al.* used colloidal gold–palladium nanoparticles to achieve the oxidation of CH<sub>4</sub> to CH<sub>3</sub>OH with high selectivity (92%) in aqueous hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) solution at a low temperature of 50 °C. It is confirmed that a considerable portion (70%) of the oxidation comes from gas-phase O<sub>2</sub>, which significantly improves the economy of the reaction.<sup>80</sup> Very recently, Mao *et al.* reported an edge-rich MoS<sub>2</sub> catalyst that could achieve direct CH<sub>4</sub> conversion to CH<sub>3</sub>OH with O<sub>2</sub> at room temperature. This catalyst showed a remarkable CH<sub>4</sub> conversion (4.2%) with high selectivity to C1 oxygenates (>99%).<sup>81</sup> The bi-Mo sites of MoS<sub>2</sub> are similar to the binuclear iron (bi-Fe) site in MMO hydroxylase which activates CH<sub>4</sub> with Fe–O species generated from O<sub>2</sub>. By simulating the biocatalytic function of MMO, a one-step direct conversion of CH<sub>4</sub> with O<sub>2</sub> at room temperature can be proposed (Fig. 6).

Photocatalytic partial oxidation of methane is in the spotlight since the discovery of CH<sub>4</sub> activation to CH<sub>3</sub>O<sup>-</sup> over TiO<sub>2</sub> in 1978.<sup>82</sup> CH<sub>3</sub>OH,<sup>83</sup> HCOH (ref. 84) and HCOOH (ref. 85)

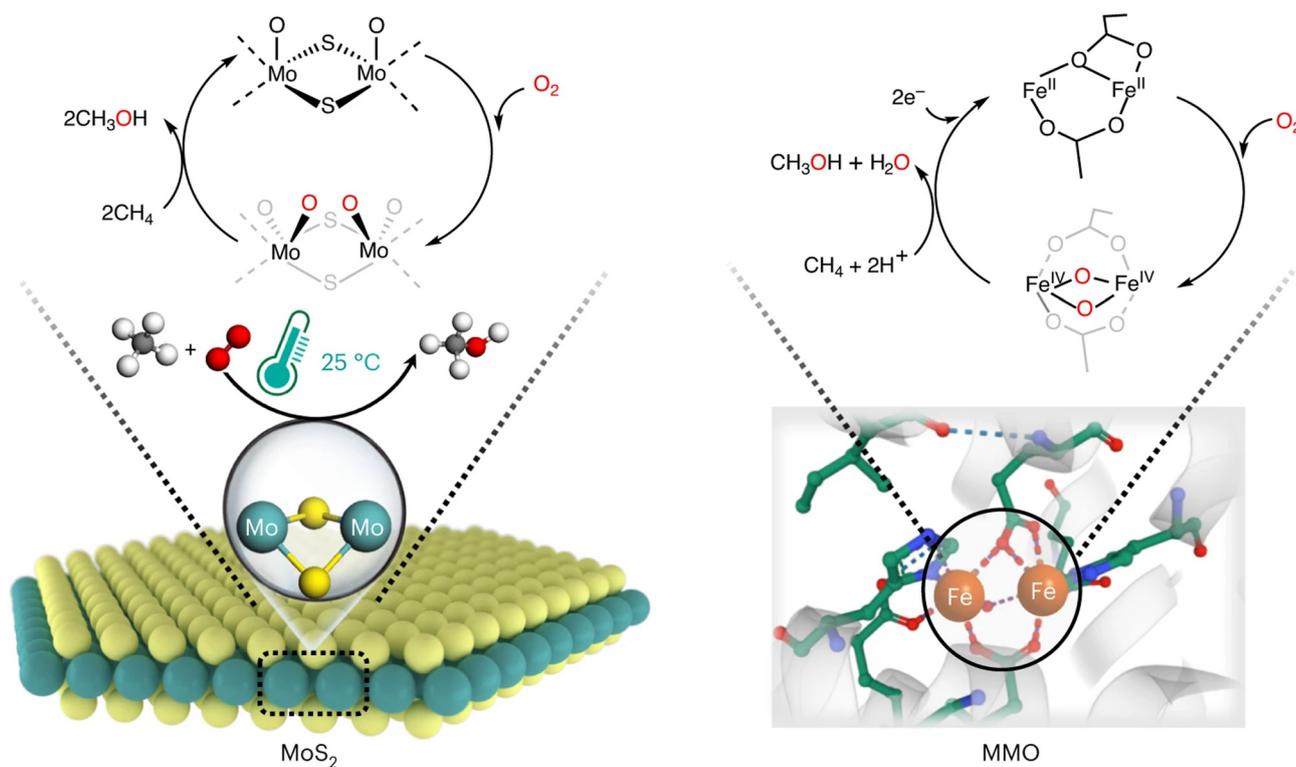


Fig. 6 CH<sub>4</sub> conversion over MoS<sub>2</sub> and MMO catalysts at room temperature.<sup>81</sup> Modified with permission from ref. 81. Copyright (2023) Springer Nature.



can be obtained as main products based on literature reports. These groundbreaking studies greatly expanded the conversion pathways of methane, but a large amount of by-products (CO, CO<sub>2</sub>) resulted in poor reaction selectivity, making it difficult to achieve industrial production. Thus, regulating the reaction conditions, including oxidant selection, photocatalyst design, reaction temperature, time, *etc.*, is crucial and difficult. Up to now, it has been reported that the activation of CH<sub>4</sub> is mainly achieved by O<sup>2-</sup> radicals, O<sup>-</sup> species (photogenerated holes), ·OH radicals, and other species.<sup>86</sup>

Electrocatalytic partial oxidation of methane to valuable chemicals and liquid fuels can occur under mild reaction conditions. Either active oxygen on the surface of the electrode directly or free radicals generated at the electrode/electrolyte contact indirectly can cause the electrocatalytic activation of CH<sub>4</sub>.<sup>87</sup> Although electrochemistry generates oxidation catalytic sites by controlling the electrode potential, methane activation is essentially a chemical step. Therefore, some electrocatalysts have metal centers similar to those of thermal catalysts, such as Pd, Pt, V, Ru, and Ir.<sup>88</sup> The electrocatalytic activation of CH<sub>4</sub> on metal oxide electrocatalysts is attributed to the dehydrogenation mechanism, while the deprotonation mechanism is considered to occur on Pd and Pt based electrocatalysts.

### 2.3 Biomass catalytic upgrading

Biomass covers a variety of biotic resources, such as crops, forestry, animals, and domestic waste.<sup>89</sup> Nowadays, biomass is considered as a renewable source. Fossil fuels like petroleum may cause irreversible damage to the local ecological environment during mining and release a large amount of CO<sub>2</sub> during utilization, causing the greenhouse effect. In contrast, CO<sub>2</sub> in the atmospheric environment can be converted into biomass by planting fast-growing forests, which can be further converted into chemicals with the assistance of catalysts. The efficient use of biomass may, therefore, have significant impacts on the production of energy and commodity chemicals.<sup>90</sup> The choice of non-edible biomass raw materials such as corn stalks will greatly reduce the waste of biomass and avoid competition with food. Currently, sono and mechanochemical,<sup>91</sup> photochemical,<sup>92</sup> and other technologies have been employed in biomass catalytic conversion.

Although biomass is more environmentally friendly, some key issues like low product selectivity and difficult separation in the transformation process will significantly increase the production cost. Products with high selectivity can be obtained through fermentation and enzyme catalysis. However, the strict production conditions and low efficiency hinder its large-scale applications. Hence, it is necessary to find feasible routes to convert biomass. The breakthrough to solve this problem lies in developing a stable, high-efficiency, and cost-effective catalytic process. In the following section, lignin upgrading and bio-aviation fuel synthesis from biomass will be briefly discussed.

**2.3.1 Lignin upgrading.** Lignocellulose is the most widely existing biomass in natural plants, which contains lignin (15–25%), hemicellulose (23–32%), and cellulose (38–50%).<sup>91</sup> These three polymers are constituted by aromatic monomers, C6/C5 sugars, and C6 sugar, respectively. For industrial production, the depolymerization of lignocellulose into three monomers for further conversion is an effective route. In particular the catalytic transformation of lignin is considered to be the most important since it is the most abundant aromatic carbon source in nature. Lignin is a complex phenolic polymer formed by sinapyl alcohol, coniferyl alcohol, and *p*-coumaryl alcohol (Fig. 7).<sup>93</sup>

Generally, the strategy for valorizing lignin is to depolymerize lignin to monomers, followed by further transformation into value-added chemicals or alternative fuels *via* catalytic upgrading. The C=C bonds in the primary building blocks of lignin provide the possibility of cross-coupling between the monomers, which is crucial for forming 3D network structures connected by ether or C–C bonds. These structures give lignin excellent mechanical properties but cause great difficulties in depolymerization. The main difficulty of depolymerization lies in finding a suitable catalyst to break the C–O and C–C bonds in the 3D network and form final products in a narrow distribution.<sup>94,95</sup> Over the past decades, numerous catalysts have been used for lignin depolymerization, such as porous carbon, zeolites, metal nanoparticles, metal–organic frameworks (MOFs), single-atom catalysts, and other functionalized catalysts.<sup>96</sup> Notably, Sels *et al.* developed an integrated biorefinery process that could convert 78 wt% of birch into xylochemicals.<sup>97</sup> The life-cycle evaluation shows that this process has a lower CO<sub>2</sub> footprint compared to the fossil-based production process.

The depolymerization products of lignin exist as a mixture of phenolic compounds. The high oxygen content in the mixture limits its utilization as fuel. Therefore, numerous approaches have been attempted in upgrading these monomers to reduce the oxygen content. Among these approaches, hydroprocessing appears to be the most frequently used and most efficient technique.

Photocatalytic conversion of lignin into fuel and other chemical raw materials is also a possible route. Under the excitation of light, the free radicals produced by a photocatalyst will react with the C–O and C–C bonds of

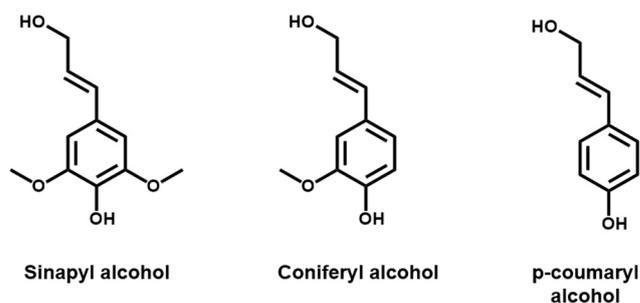


Fig. 7 Composition of lignin.



lignin. Generally, photocatalysts tend to select C–O or C–C bonds for cleavage rather than break all bonds. As for C–O bond cleavage, a two-step redox-neutral strategy and a one-step photoredox-neutral strategy have been proposed.<sup>98</sup> However, breaking the C–O bond can only reach 50% of the theoretical yield.<sup>99</sup> Value-added oxygen compounds can be obtained through C–C bond cleavage, while only a small amount of catalyst selectively breaks C–C bonds due to the higher bond dissociation energy.

**2.3.2 Biomass to bio-aviation fuels.** The sustainable development of the aviation industry has received global attention due to the significant emissions of CO<sub>2</sub> and the high dependence on fossil fuels. Biomass aviation fuels are considered as a promising alternative to traditional aviation fuels. The raw materials of bio-aviation fuels can be derived from oil crops, lignocellulose, sugar, and starch biomass.

Different technologies can be used to produce bio-aviation fuels, and the existing main conversion pathways for bio-aviation fuel technology are summarized in Fig. 8, including alcohol to jet (ATJ), oil to jet (OTJ), and gas to jet (GTJ).

**Alcohol to jet fuel.** ATJ technology consists of two main stages, namely alcohol production and alcohol conversion. The most common method for alcohol production is the biological fermentation of sugars. It can also be obtained through starch hydrolysis and fermentation. The second stage of ATJ is to convert alcohols as basic raw materials into long-chain hydrocarbons, including i) alcohol dehydration to olefins, ii) olefin catalytic oligomerization to intermediate fractions, iii) middle fraction hydrogenation to alkanes, and iv) aviation fuel production by distillation.<sup>100</sup>

In industry, ethanol, butanol, and isobutanol are generally used as intermediate products to be converted into fuel. Ethanol dehydration to ethylene is already a mature process. In this step, commonly used catalysts are Al<sub>2</sub>O<sub>3</sub>, transition

metal oxides, zeolites, and heteropolyacid catalysts.<sup>101</sup> Water is generated during alcohol dehydration to olefins, so the catalyst for this process should be water-resistant. For oligomerization processes, both homogeneous and heterogeneous catalysts can be employed. Zeolites are widely used in oligomerization processes, while the problem of easy coking and deactivation is still difficult to solve. The products from different alcohols vary slightly. Butanol dehydration oligomerization yields compounds such as C<sub>8</sub>, C<sub>12</sub>, and C<sub>16</sub>, while ethylene yields a wider range of compounds.<sup>102</sup> The olefins obtained from oligomerization are hydrogenated to obtain saturated alkanes, which are finally distilled to obtain aviation fuel.

**Oil to jet fuel.** OTJ is a process of hydrogenation of triglycerides, saturated and unsaturated fatty acids in vegetable oil, food waste oil, and animal fat.<sup>100</sup> The process is generally divided into three stages.<sup>103</sup> The first stage is to convert unsaturated fatty acids and triglycerides into saturated fatty acids through catalytic hydrogenation, where triglycerides are converted into saturated fatty acids through the  $\beta$ -hydrogen elimination reaction. The second stage is to convert saturated fatty acids into straight chain alkanes of C<sub>15</sub>–C<sub>18</sub> through hydro-deoxygenation and decarboxylation reactions.<sup>100</sup> In early studies, precious metal catalysts supported on zeolites or oxides were mainly used. Due to the susceptibility of precious metal catalysts to poisoning and deactivation, generation of cracking products, and high cost, the research focus has gradually switched to transition metals such as Ni, Mo, Co, and supported bimetallic catalysts.<sup>104</sup> The third stage is cracking and isomerization reactions, where deoxygenated straight chain alkanes are further selectively hydrocracked and deeply isomerized to generate highly branched alkanes. The commonly used catalysts for this stage are Pt loaded on Al<sub>2</sub>O<sub>3</sub> or

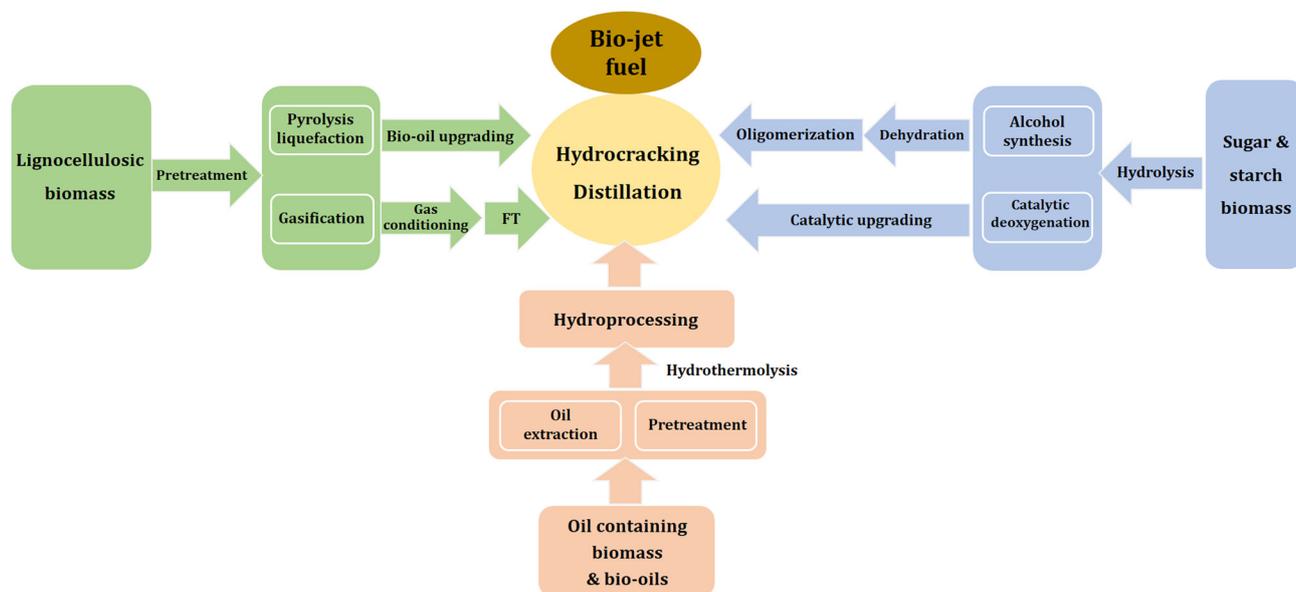


Fig. 8 Complete processes for the production of bio-jet fuel.



zeolites.<sup>105,106</sup> Finally, the mixed liquid fuel is separated into light gases, naphtha, and bio-aviation fuel through a distillation process. The main product produced by OTJ is biodiesel, which accounts for approximately 15% of the total product. The proportion of bio aviation fuel can be increased by changing the distillation temperature or further cracking.

Aviation fuel prepared by OTJ has advantages such as high thermal stability, good cold fluidity, high cetane number, and low exhaust emissions. However, its low aromatic content will lead to low fuel lubricity and leakage problems.<sup>107</sup> The lignin can be selectively transferred to aromatics and cycloalkanes through hydrodeoxygenation and blended into the aviation fuels produced from OTJ to increase the aromatic content.<sup>108</sup> The catalysts for this reaction should have suitable acid sites to remove the methoxy groups and also have metal sites for hydrogenation of aromatic rings and removal of hydroxy groups.

*Gas to jet fuel.* Fischer-Tropsch (FT) reactions produce liquid hydrocarbon fuels from syngas. Coal, natural gas, biomass, and urban solid waste can all be used to produce syngas. Among them, biomass and urban solid waste are more environmentally friendly raw materials. The process of FT producing bio aviation fuel can be divided into six steps, namely i) raw material pretreatment, ii) biomass gasification, iii) gas regulation, iv) acid gas removal, v) FT synthesis, and vi) crude oil refining.

The quality of syngas has a significant impact on FT synthesis. Raw materials from biomass usually have high oxygen content and contain various pollutants. Therefore, the purification of syngas is crucial. During gasification, many factors, such as temperature, gasification agent, biomass type, particle size, heating rate, operating pressure, equivalence ratio, and reactor configuration, can affect the yield and composition of syngas. The gasification process is carried out under high-purity oxygen and high-temperature steam (about 1300 °C). The ideal ratio of H<sub>2</sub>/CO for FT synthesis is 2/1. However, for the synthesis gas prepared from biomass, the H<sub>2</sub>/CO ratio is generally between 0.6 and 0.8, so it is necessary to adjust the H<sub>2</sub>/CO ratio through hydrogenation. Unconverted syngas and some FT gas can be recycled to FT reactor after reforming. Liquid products are refined to obtain different types of fuels. Excess gas can be used for power generation. FT fuel is usually sulfur-free and nitrogen-free and has high thermal stability. The disadvantages are low aromatic content and low energy density.<sup>100</sup>

*Comparison of main bio-aviation fuel technology routes.* The above-mentioned production technologies for biofuels can be generally summarized into two processes, namely pre-deoxidation and post-upgrading. The biggest difference among the three production routes lies in the differences in the modified raw materials. Herein, the modified raw materials are referred to as “crude products”. From a chemical composition perspective, the “oil potential” raw materials of OTJ and FT routes are alkanes, which have a similar composition to aviation fuel. Compared with ATJ and OTJ technologies, the FT route requires breaking the C–C

and C–H bonds in the raw materials first and then regenerating them in FT synthesis. From the perspective of the chemical bond economy, the FT route, *i.e.*, GTJ, has poor economic efficiency.

## 2.4 Plastic conversion and recycling

Plastics, including polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC), polystyrene (PS), polyethylene terephthalate (PET) *etc.*, are irreplaceable in our daily lives. In the past decades, plastics have been widely employed as packing materials due to their intrinsic properties of low cost, long durability, and light weight. In the future, plastics will be more widely used in electronic products, transportation vehicles, medical care, construction, and other aspects. However, most of these polymers take several centuries to degrade under natural conditions and cause severe “white pollution”. Because it is difficult to digest and metabolize, wild animals can die after eating plastics. It is worth noting that the microplastics (defined as ≤5 mm) and nano-plastics produced during the degradation process can be easily ingested by animals and ultimately enter the human body.<sup>109</sup> Various methods have been applied to the post-treatment of plastics, including landfill, incineration, catalytic degradation, and biodegradation (Fig. 9).<sup>110</sup> It has been found that some marine fungi tend to eat certain types of plastics,<sup>111</sup> although it is a drop in the bucket. With the help of catalytic degradation, plastics can be converted into fuel and chemical raw materials, thus realizing recycling.

The technologies for converting plastic waste into energy can be divided into mechanical recycling and chemical recycling. Mechanical recycling, like heat melting, is a common way of plastic recycling, while only a part of thermoplastics can be recycled in this way. Chemical recycling can depolymerize waste plastics into monomers which can be used to make plastics or other materials. In general, plastics are composed of “short-range chain”, “long-range chain”, and “condensed matter” structures.<sup>111</sup> The short-range chain structure is the decisive factor in selecting the recovery method. Understanding long-chain and condensed matter structures is crucial for optimizing the selected recycling processes and improving selectivity as well as yield. Chemical recycling can be roughly summarized as thermal pyrolysis, co-pyrolysis, hydro/solvopyrolysis, and enzymatic recycling. In recent years, pyrolysis has been recognized as an appropriate approach for recycling plastics, which does not cause much water waste or contamination. Extensive research has been conducted to convert waste plastic into an alternative form of energy through thermochemical conversion processes.<sup>112</sup> Most work has focused on thermal and catalytic pyrolysis. For thermal pyrolysis, pressure, temperature, and reaction time can alter the distribution of pyrolysis product components. The microscopic mechanism has not been clearly elucidated yet.<sup>113</sup> Co-pyrolysis is one form of thermal pyrolysis. For example, co-pyrolysis of biomass and plastics can produce



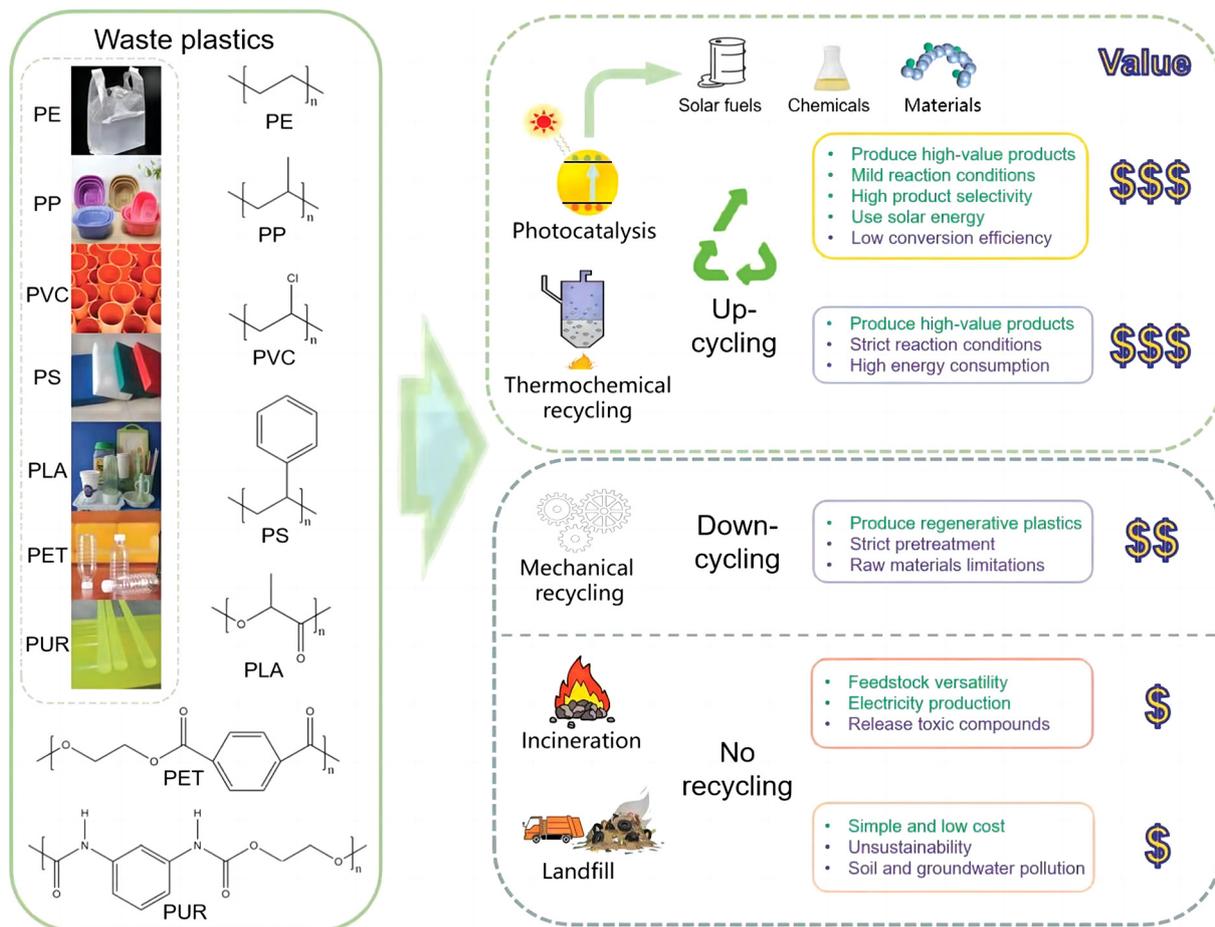


Fig. 9 Methods for plastic degradation.<sup>110</sup> Modified with permission from ref. 110. Copyright (2022) John Wiley & Sons.

hydrocarbons similar to fuel oil, aromatic hydrocarbons, lubricants, and other chemicals.<sup>114</sup> The thermal pyrolysis process produces low-quality liquid oil containing impurities at high temperatures. In contrast, catalytic pyrolysis has higher potential to convert plastics into liquid oil at lower temperatures and with less reaction time. Catalysts are the most important influencing factor in this process, which can change the species and proportion of the final products. The most commonly used catalysts are solid acid catalysts, such as zeolites.<sup>115</sup> Different catalysts have completely different decomposition abilities for different kinds of plastics. It is difficult to find a universal catalyst that can effectively decompose all plastics. Hydropyrolysis and solvolysis have also been used for bond cleavage in plastic waste, which are able to break the C–C and C–H bonds at lower temperatures. Microwave catalysis is considered as a promising strategy, because microwave can cause the overall temperature rise of plastic to break bonds under mild conditions.

In recent years, in addition to the pyrolysis of plastics under harsh conditions, emerging catalytic systems such as photocatalysis and electrocatalysis have also been proposed for plastic conversion.<sup>116</sup> Converting plastic waste into industrial raw materials under mild conditions is more energy-saving and environmentally friendly, which is

consistent with the concept of sustainable development. For example, plastics can be degraded by free radicals produced by photocatalysts under light exposure.<sup>117</sup> The advantage of the photocatalytic degradation of plastics is that the solar energy is infinite, while the reaction often has a low conversion and produces superabundant CO<sub>2</sub> as an undesired product. The most commonly used photocatalyst is TiO<sub>2</sub>, which can degrade various plastics, including PE, PVC, PS, *etc.* However, these studies show that plastics (mostly PE and PS) are only partially converted, which may produce microplastics or nano-plastics and cannot fully address the pollution issue. Electrocatalysis has also been applied in plastic transformation.<sup>118</sup> The main advantage of electrocatalysis is room temperature reaction with no corrosive conditions. The electrocatalytic recycling of waste plastic leads to a low depolymerization rate due to the low solubility of plastic in aqueous solution.

The enzymatic recycling of plastics has also attracted extensive research attention. In 2016, Yoshida *et al.* reported a bacterium that could degrade almost 100% of PET films after 6 weeks with the help of a two-enzyme system.<sup>119</sup> Enzyme-catalyzed plastic conversion is mainly focused on polyester plastics such as PET.<sup>120</sup> The activity of an enzyme depends on the active site, substrate binding, and protein structure. Among



these, substrate binding is the rate-limiting step of the restricted enzyme. Enzymes can be randomly bound to long chains or chain-ends and catalyze depolymerization, which will directly convert polyester plastics into value-added products like monomers. Structure-guided protein engineering of PET hydrolases has a significant contribution to improving the catalytic performance. Two major challenges lie in enzymes for catalysis, namely improving the stability of enzymes and realizing the direct processability of crystalline post-consumer PET. Besides, the actual treated wasted plastics usually contain multiple types of plastics, meaning it is almost impossible to treat all plastics in a single enzymatic way.

There is an urgent need to solve the problem of white pollution. The traditional thermal transformation might cause more pollution to the environment, and the product distribution has great limitations. The catalytic conversion under mild conditions produces less pollution and consumes less energy. However, eligible techniques for the catalytic conversion of plastics are still in their infancy and need further improvements. Overall, plastic catalytic recycling can produce fuel or chemicals, with chemicals being more valuable and more desirable products than fuel. The use of plastic-derived chemicals can reduce the consumption of fossil resources and thereby contribute to the sustainable development of the energy system. For the direct conversion of plastics (halogen-free) to fuel, a simple and mature strategy is refining together with crude oil. The bottleneck of this strategy currently lies in the collecting and sorting of plastics.

### 3 Prospect

With the development and progress of human society, sustainable energy sources are urgently desired as alternatives to traditional fossil fuels. While sustainable energy has many advantages, it faces various challenges such as energy storage, intermittency, and infrastructure upgrades. Besides, the cost of many sustainable energy technologies remains too high, limiting their application on a large scale. Catalysis plays a vital role in the regeneration and utilization of renewable energy by improving the distribution of reaction products and reducing the energy input. Herein, some representative examples of catalysis for sustainable energy, namely methane catalytic conversion, biomass catalytic upgrading, hydrogen energy, and plastic chemical recycling, are briefly discussed. Various catalytic technologies, including thermocatalysis, photocatalysis, electrocatalysis, and biological catalysis, have already shown great potential in this emerging field. Although those new ways of developing sustainable energy have great promise, they are still facing great challenges, and the main challenges are even basically common for different energy carriers.

Methane conversion and reforming can reduce greenhouse gas emissions, promote energy diversification, and improve resource utilization efficiency. However, existing catalysts are insufficient to support conversion occurring at low temperatures and pressures, resulting in the production of a large number of by-products and a significant increase

in costs. Biomass catalytic upgrading can convert agricultural, forestry, and industrial waste into useful energy or products, effectively reducing the accumulation of waste and mitigating environmental pollution caused by landfill and incineration. Although biomass upgrading has a long history of development, there are still some technical bottlenecks, especially in terms of conversion efficiency. In addition, some biomass upgrading processes still generate pollutants and greenhouse gases such as methane, which have a certain degree of pollution to the environment. Hydrogen, as a promising clean energy source, has significant advantages such as zero emissions, high energy density, and wide applications. It is an important component of the future low-carbon economy and sustainable energy system. The high production cost, low hydrogen storage density, poor safety, and inadequate infrastructure of hydrogen still constrain its large-scale application. Plastic conversion and recycling have significant advantages in reducing pollution, conserving resources, lowering carbon emissions, and promoting economic cycles. However, its technological bottleneck greatly limits its application, especially in terms of the recycling of some complex plastics, recycling costs, environmental pollution control, and other issues that still need to be further addressed.

Due to the immaturity of new technologies and the fact they are still under research, it is inevitable that there are some thorny problems such as high cost, poor infrastructure, incomplete establishment of raw material supply chain, limited public awareness and acceptance of new technologies.<sup>121</sup> These issues are obstacles to the promotion of sustainable energy, yet they are not unsolvable. Research and development of new catalysts and efficient processes are essential to reduce costs, enhance infrastructure development, and improve cooperation and resource integration across different fields. By addressing these common issues, sustainable energy is expected to achieve faster development and wider applications. It is foreseeable that, with indispensable help from catalysis, sustainable energy will become a great success in promoting the harmonious development of energy, environment, and human society.

### Data availability

No primary research results, software or code have been included and no new data were generated or analysed as part of this review.

### Conflicts of interest

The authors declare no conflict of interest.

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