Recent Progress in Materials Exploration for Thermocatalytic, Photocatalytic, and Integrated Photothermocatalytic CO₂-to-Fuel Conversion

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The excess depletion of carbon-rich fossil fuels and agroforest biomass resources has aggravated the energy crisis and environmental pollution, causing increased CO₂ emissions. Accordingly, the goal of “peak CO₂ emissions and carbon neutrality” is proposed to alleviate global warming. CO₂-to-fuel conversion is considered as a preferable move for reducing the atmospheric CO₂ concentration and further upgrading to chemical feedstocks. However, the highly efficient CO₂ conversion remains challenging due to the thermodynamic limits and kinetic barriers, which require high energy input through conventional thermocatalysis. Inspired by “artificial photosynthesis,” photocatalytic CO₂ transformation has received tremendous attention and makes remarkable progress over the past decades, although it is still far from practical application. Recently, the integrated photothermocatalysis has emerged as an intelligent strategy to utilize solar energy to induce local heating and energetic hot carriers, which synergistically promote CO₂-to-fuel conversion. The key to the success of CO₂ upgradation is catalysts’ development with improved activity, selectivity, and stability. This review highlights the recent advancements in materials designing for practical CO₂ conversion through thermocatalysis, photocatalysis, and photothermocatalysis during the past five years, emphasizing the reaction pathways and mechanism on the C═O bond activation and intermediates formation. Finally, the current challenges and future opportunities are described.

1. Introduction

Since the rapid development of the national economy, energy consumption has been continuously increasing in the past decades. The excessive dependence on nonrenewable fossil fuels has released large amounts of carbon dioxide (CO₂), which is a notorious greenhouse gas and has certainly caused serious global warming and ocean acidification problems. In response to the challenges of climate change, the entire world has put forward the goal of “peak CO₂ emissions and carbon neutral.” As an important part of the Paris Agreement commitment, a roadmap for China to “double carbon” target is to reach a carbon peak emission by 2030 and be carbon neutral by 2060. Particularly, carbon emission reduction has become a critical path to realize green development and achieve the “double carbon” vision. Accordingly, minimizing atmospheric CO₂ concentrations to alleviate environmental pollution and climate change has become an imperative mission. The imposition of the CO₂ tax is an effective initiative to realize the energy conservation and emission reduction as well as the optimized energy mix, which has been carried out by an increasing number of countries according to their national conditions. In addition, CO₂ capturing and utilization through chemical transformation has been considered as a preferable process for highly efficient CO₂ mitigation rather than separation and geological sequestration processes.[1] Importantly, it provides
an economical manner to convert CO₂ into high-value-added products, which can be manufactured into chemicals and fuels on an industrial scale, thus closing the carbon loop. However, the CO₂ molecule is kinetically inert and thermodynamically stable, which requires effective catalytic techniques to decrease reaction barriers in C=O activation and C–O cleavage. Thus, the CO₂ conversion requires substantial energy inputs, including heat and sunlight, which could achieve sufficient reaction rates for highly efficient and selective CO₂ transformation through thermocatalytic and photocatalytic approaches. Moreover, photothermocatalysis as the combination of two energy sources in one reaction process has been regarded as an advanced approach, which further enhances the catalytic performance of CO₂-to-fuel conversion. The chronology of the technologies for CO₂ conversion is presented in Figure 1, highlighting the milestones of the developments of catalysts, products, and techniques for their characterization.

Among these technologies, thermocatalytic transformations of CO₂ either via direct or indirect approaches have already been applied at the industrial level and have relatively higher product outputs. Four main classes of products can be obtained from CO₂ thermocatalysis, that is, carbon monoxide (CO), methanol (MeOH), methane (CH₄), and other higher hydrocarbons. Cheap and clean hydrogen (H₂) from an economical and sustainable route is critical to have a positive environmental impact on the aforementioned CO₂ thermocatalytic processes. First, CO generated from reverse water-gas shift (RWGS, CO₂ + H₂ → CO + H₂O) has been considered as a valuable catalytic process for CO₂ hydrogenation as CO is an important feedstock for Fischer-Tropsch and MeOH synthesis (CO₂ + 3H₂ → CH₃OH + H₂O). Second, a large proportion of *CO ("*" represents "the surface adsorption site on catalyst") absorbed on the catalyst surface could suppress the competing RWGS route, thus generating a higher-value-added product—methanol. Third, the methanation of CO₂, also called the Sabatier reaction (CO₂ + 4H₂ → CH₄ + 2H₂O), undergoes an eight-electron process for the formation of syngas and compressed natural gas. Finally, the direct hydrogenation of CO₂ into other hydrocarbons, including light alkanes and olefins, is similar to that of the FT process through the methanol-mediated or nonmethanol-mediated pathways.

However, CO₂ utilization through thermocatalytic processes requires high energy costs accompanied by additional CO₂ emission, as the heat was mainly obtained from the combustion of fossil fuels. By comparison, photocatalysis driven by renewable solar energy is an attractive approach and serves as an effective alternative for CO₂ transformation, which has already been at a stage of rapid development. Under solar light irradiation, semiconductor photocatalysts could accelerate the C=O activation process, which could be subsequently reduced to hydrocarbons by photogenerated electrons. Unfortunately, the practical application of photocatalysis has yet reached an industrial scale due to the lack of highly effective photocatalysts, limited photocatalytic performance, suboptimal reactors, and the intermittent nature of solar light. Therefore, the integration of light and heat in CO₂ chemical transformations emerges as a promising approach to further reduce the consumption of fossil fuels and increase the conversion efficiency of atmospheric CO₂. Photothermocatalysis absorbs the visible and near-infrared light
energy, which undergoes the dissipation into heat (temperature up to 300–500 °C or even higher), thus inducing a process similar to conventional thermocatalysis. The photothermo effect can be ensured by the construction of efficient light-absorbing materials to capture heat from sunlight and raise the temperature of the whole reaction system. Another way is to synthesize plasmonic metals to cause surface plasmon resonance (SPR) effects, which could generate numerous hot electrons and holes. There are two categories of mechanisms and applications focused on plasmonic nanostructures: 1) photoinduced hot carriers (plasmonic photocatalysis) and 2) light-excited phonons (photothermal catalysis).

Accordingly, the plasmonic photothermocatalytic behavior provides a preferable understanding of electron-driven and temperature-driven catalysis over plasmonic materials, which is conducive to bridge the gap between the application of thermocatalysis and photocatalysis. Thereby, RWGS, methanation, methanol, and other hydrocarbons synthesis routes can be realized in a highly active and selective manner. Meanwhile, Ozin et al. proposed universal equations, which could describe net CO₂ emissions induced from (photo)thermocatalysis RWGS and methanation synthesis in batch and flow reactors. With archetype model systems, some factors of the final amount of effluent CO₂ can be concluded, which provided a promising guide for the rapid development of (photo)thermocatalytic CO₂ conversion using sunlight as the clean and sustainable energy source. In Figure 2, we summarize the major properties of the technologies for thermocatalytic, photocatalytic, and photothermocatalytic CO₂ conversion, highlighting the differences in reaction routes, products, advantages, and disadvantages of each technology.

Nowadays, the published reviews on CO₂ reduction mainly concentrated on a certain technology (e.g., thermocatalysis, photocatalysis), while a few have emphasized the integration of thermo- and solar energy in catalysis. Considering the rapid and fascinating scientific research that have been sprung up in these important and hot topics, we herein present a comprehensive and timely review of the recent advances in thermo-, photo-, and the integrated photothermocatalytic CO₂ conversion to high-value-added chemicals and fuels during the past five years, aimed at highlighting the differences and similarities between solar- and thermo-driven catalysis in depth. The motivation and fundamentals of each catalytic technology are first introduced, followed by the emphatic discussions on their recent progress toward small molecules (e.g., formate, CO, CH₄, and alcohols) and fine chemical (e.g., C₂+ olefins and oxygenates) synthesis. It mainly provides objective assessment on the merits and demerits of catalysts, in terms of catalytic activity, selectivity, and stability. Then, distinct catalytic mechanisms for these technologies are summarized to provide a comprehensive understanding of C=O activation and intermediate adsorption, which has been realized by the advanced studies of in situ/operando characterizations and theoretical calculations. Finally, the current challenges and future perspectives for the efficient utilization and upgradation of CO₂ into value-added products are addressed in these flourishing fields. Thus, this review provides horizontal comparisons by discussing different catalysts or reaction pathways for the same product. In parallel, this review provides vertical comparisons of the recent advances in catalytic technologies for CO₂ conversion. As a result, this review is expected to be an essential work to provide important references related to the chemical transformation of CO₂ into chemical feedstocks with explicit directivity.

2. Thermocatalysis

2.1. Motivation and Principles

Considering that CO₂ is a thermodynamically stable molecule, high pressures and temperatures are always required to achieve...
C=O activation in the chemical conversion of CO₂-to-chemicals/fuels. Thermocatalysis driven by heat energy performs high efficiency and applicability for the mass-produced synthesis of fine chemicals (hydrocarbons, olefins, and NH₃, etc.) in conventional industrial manufacture. Accordingly, thermocatalytic CO₂ conversion has been an ideal candidate to generate high-value-added carbonaceous compounds, which mainly involve hydrogenation reactions with a CO₂ flow over catalysts at controllable temperatures and pressures. In the CO₂ thermocatalysis process, CO₂ molecules first adsorb on the surface of catalysts, and then essential activation energy (Eₐ) is required to bond C=O chemical bonds. Subsequently, another activation energy barrier should be overcome for the formation process of intermediates, where H₂ is directly used as the reductive reagent and *H donor. Finally, the interactions between intermediates and the catalyst surface influence the desorption ability of product molecules, which would exhibit different selectivities for C₁ chemicals or more valuable C₂+ chemicals by regulating C–H bonding or C–C coupling. As shown in Figure 3a, the reaction process of CO₂ hydrogenation should overcome excessive energy barriers without the presence of catalysts (solid line), which need enough thermal energy to match to overcome the activation energy Eₐ1 of the elemental step. Thus, the development and employment of highly efficient catalysts is the key to accelerate the CO₂ conversion rate by lowering the Eₐ2 and Eₐ3 values (dashed line). In this regard, four main reaction pathways on thermocatalytic CO₂ conversion have sprung up in the recent 5 years, especially in the field of heterogeneous catalysis.

2.2. Plausible Routes for CO₂ Hydrogenation

Hydrogen is a high-energy carrier, which can be used to hydrogenate CO₂ into the products of CO, MeOH, CH₄, and other hydrocarbons (Figure 3b). The related reaction pathways are described as follows.

2.2.1. CO₂ to CO: Redox versus Associative Pathway

CO₂-to-CO conversion via RWGS reaction has been regarded as a promising route for CO₂ hydrogenation, which is an endothermic reaction driven by certain temperatures and pressures. The reaction mechanisms have been generally classified into redox and associative mechanisms. 1) In a redox reaction, H₂ acts as a reductive reagent instead of a participant for the generation of intermediates. For example, Cu species supported on transition metal oxides/carbides (TMCs) has always been the popular alternatives for highly active and selective RWGS reactions. Cu⁰ is first oxidized by CO₂ molecules to form Cu¹ and CO, and then Cu⁺ can be reduced by H₂ to generate H₂O. The redox mechanism can be modeled as follows.

\[
\text{CO}_2 + 2\text{Cu}^0 \rightarrow \text{Cu}_2\text{O} + \text{CO}
\]

(2)

\[
\text{H}_2 + \text{Cu}_2\text{O} \rightarrow 2\text{Cu}^0 + \text{H}_2\text{O}
\]

(3)

Inspired by the abovementioned redox process, Konsolakis et al. employed Cu/Co₃O₄ as the catalyst and conducted thermodynamic analysis, realizing high CO₂ conversion (52%) and CO selectivity (95%) at 380 °C and ambient pressure. Other Cu-based materials, such as Cu/ZnO and Ru-decorated Cu/ZnO-Al₂O₃ catalysts, were also ideal alternatives for the activation and dissociation of CO₂ in the RWGS reaction. Compared with traditional metal oxide-supported Cu-based catalysts, Ma and co-workers synthesized highly dispersed Cu over β-Mo₂C (1.3 wt% Cu/β-Mo₂C) catalyst, which performed superior CO₂ conversion rate (47.7 × 10⁻⁵ mol_{CO₂} g_{cat}⁻¹ s⁻¹) and extraordinary CO selectivity (99.2%) during a 40 h test (Figure 4). The optimized activity and stability are attributed to the synergistic effect between Cu and β-Mo₂C, which contributed to the high dispersion of active Cu sites. During a redox reaction, the CO products were generated from CO₂ dissociation, while the oxygen atoms extracted from the CO₂ molecules were finally reduced by H₂ to produce H₂O. Consistent with the experimental results, the proposed reaction mechanism obtained via transient analysis suggests that the CO₂ adsorption/activation

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Figure 3. a) Energy diagram of the thermocatalytic reaction process. Eₐ1, Eₐ2, and Eₐ3 indicate the activation energy for reactants and intermediates during the different reaction progresses of CO₂ hydrogenation. The solid and dashed lines illustrate the progress of the chemical reaction without and with the presence of a catalyst, respectively. Reproduced with permission. Copyright 2019, Wiley-VCH GmbH. b) Four main products from thermocatalytic CO₂ hydrogenation reactions.
on the Cu sites is a rate-determining step, while the subsequent reduction of the adsorbed oxygen atoms of *CO2 or hydroxyls of *COOH finally produces CO or H2O molecules. Therefore, the introduction of metallic Cu is a promising way to lower the Ea of the rate-limiting step, which is conducive to the redox process.[16] The catalytic performance of the RWGS reaction via the redox mechanism can be further improved by some other strategies, such as alloying and constructing high-surface-area or nanostructuring catalysts. Reina’s group reported that saponite-supported NiCu catalysts exhibited preferable selectivity for the formation of CO (≈80%) when compared with the saponite-supported NiCo and Ni catalysts.[17] As evidenced by X-ray photoelectron spectroscopy (XPS) results, an electronically rich Ni–Cu interface contributed to the effective CO2 activation process. Furthermore, inverse nanoporous Cr2O3/Cu,[18] nanotube-structured TiO2/Cu,[19] and double-shell nanofiber-structured CuSiO/CuO[20] presented strong metal-support interactions and offered abundant surface active sites for CO2 activation and H2 dissociation in CO2-to-CO conversion. 2) In an associative pathway, metal oxides-supported metal catalysts are extensively employed as the active materials for CO2 hydrogenation into formate intermediate and the subsequent C=O bond cleavage to CO product. For example, Au-supported on γ-Al2O3 catalyst achieves high selectivity for CO formation (>99%).[21] The hydrogenation of CO2 to formate intermediates on Au sites and subsequent C=O bond breakage to CO product on γ-Al2O3 support were confirmed by diffuse reflectance infrared Fourier transform spectroscopy (DRIFT) measurement. Other metals (Pd or Ni) decorated on Al2O3 support catalyst[22] also display high activity as the formate intermediates can easily adsorb on these metal sites determined by the preferable H2 dissociation and H adsorption capabilities. However, Ag exhibits inferior activity in RWGS reaction when compared with other metals. Hence, Kim et al. adopted in situ surface analysis and density functional theory (DFT) calculations to investigate the role of Ag sites. The results demonstrated that the absorbed carbonate species on the Ag surface hinders H2 dissociation and H adsorption for CO production and thus hardly reach the thermodynamic conversion limit.

2.2.2. CO2 to MeOH: CAMERE versus Formate Pathway

CO2 to MeOH is an ideal application for large-scale MeOH production, which is extensively used as transportation fuel or as a building block for other high-value-added liquid fuels. It is an exothermic reaction that can proceed at a relatively low temperature.
temperature and a high pressure with the assistance of effective catalysts.

\[ \text{CO}_2 + 3\text{H}_2 \leftrightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O}, \Delta H_{298K} = -49.5 \text{ kJ mol}^{-1} \] (6)

Two different mechanisms were proposed in the published literature,\[^{[23a,b]}\] as illustrated in Figure 5a. One pathway that undergoes the RWGS reaction with CO acts as the reaction intermediate (CAMERE pathway) and then hydrogenates to MeOH via the conventional syngas-to-MeOH process (CO + 2H\(_2\) → CH\(_3\)OH). A recent study over nanointermetallic InNi\(_3\)Co\(_{0.5}\) first converted CO\(_2\) into CO\(_*\)\[^{[24]}\], which was then selectively hydrogenated into CH\(_3\)OH below 300 °C through CAMERE pathway, evidenced by DRIFT analysis (Figure 5b). Meanwhile, investigated by DFT analysis, the adsorbed CO\(_2\)* easily converted into CO* with a low \(E_a\) (0.32 eV) through an exothermic process \(\Delta H_{\text{reaction}} = -0.38 \text{ eV}\), which is preferable for the formate or carboxylate pathway. In addition, DFT calculations over Pd/TiO\(_2\) catalyst also demonstrated that the CAMERE pathway is the primary route for MeOH production, and CO*-

![Figure 5](image-url)
HCO\(^\circ\) conversion is the rate-determining step.\(^{25}\) The other pathway proposes that the first step of MeOH synthesis is the direct CO\(_2\) hydrogenation through formate (HCOO\(^\circ\)) or carboxylate (COOH\(^\circ\)) intermediate, and the subsequent formate/carboxylate hydrogenation is regarded as the rate-determining step (formate pathway).\(^{26}\) In situ DRIFT measurement confirmed that CO\(_2\) was first activated and converted into HCOO\(^\circ\) intermediate at a relatively low temperature in the presence of CoN nanosheets and then generated CH\(_2\)O\(^\circ\) species with a further increase of reaction temperature.\(^{27}\) Atomic Pt embedded in MIL-101 shows high turnover frequency (TOF) (117 h\(^{-1}\)) and optimal selectivity for MeOH production (90.3\%) at 150 °C and 32 bar during CO\(_2\) hydrogenation.\(^{28}\) The Pt single atom and coordinated O atom synergistically contributed to H\(_2\) dissociation and O–H formation. Afterward, the H atom in the O–H group combined with CO\(_2\) to generate HCOO\(^\circ\) intermediate. For neighboring Pt monomers,\(^{29}\) CO\(_2\) was first hydrogenated into formic acid (HCOOH) via the transformation of COOH\(^\circ\) intermediate. The successive steps involve the HCOOH hydrogenation into CH(OH)\(^\circ\), CHOH\(^\circ\), and CH\(_2\)OH\(^\circ\) intermediates and finally MeOH. The above reaction pathways effectively lower the activation energy and enhance the catalytic activity, which result in the preferable selectivity for MeOH production.

When referred to catalysts, Cu-based materials and metal oxide supports have been commonly applied in MeOH synthesis. In these catalysts, Cu serves as the main active component, whose performance can be enhanced by the incorporation of other elements (Zn, Al, Mg, Ca, Sr, Ba, Zr, Ti, F, etc.). The commercial Cu/ZnO/Al\(_2\)O\(_3\) catalyst presents high selectivity and activity toward MeOH production by CO\(_2\) hydrogenation, with the intermediates of HCOO\(_\bullet\), H\(_2\)COO\(_\bullet\), H\(_2\)COOH\(_\bullet\), CH\(_2\)O\(_\bullet\), and CH\(_3\)O\(_\bullet\).\(^{30}\) However, the severe reaction conditions (200–400 °C or 20–100 bar) largely impede the economic feasibility of this technology. Delightedly, a low-temperature (120–170 °C) CO\(_2\)-to-CH\(_4\)H\(_2\)O conversion with nearly 100% yield was realized using tertiary amine and alcohol through the condensed-phase hydrogenation of alkylcarbocation, accompanied by the generation of ammonium formate and alkylformate intermediates.\(^{31}\) The incorporation of alkaline metal oxides (e.g., MgO, CaO, SrO, and BaO) into Cu/Al\(_2\)O\(_3\) catalysts contributes to a higher Cu\(^{\text{II}}\)/Cu\(^{\text{IV}}\) ratio and surface area, which shows a higher MeOH production rate and suppress the competing RWGS reaction.\(^{32}\) Evidenced by DFT, DRIFT, and kinetic Monte Carlo (KMC) simulations, the reduced Zr\(^{\text{IV}}\) sites at the interface of Cu/ZrO\(_2\) preferably absorb the *CO\(_2\), *CO, *HCO, and *H\(_2\)CO intermediates, which moderately promote methanol synthesis on Cu.\(^{33}\) In this work, TiO\(_2\) can also enhance MeOH production on Cu via the RWGS pathway with carboxyl intermediates. Meanwhile, the formation rate of *H\(_2\)CO is independent of the formation rate of *HCOO\(_\bullet\), suggesting that the CO\(_2\)-to-MeOH conversion does not follow the formate pathway for both catalysts. As the synergetic effect of Cu and ZnO is non-negligible in CO\(_2\) hydrogenation, the ternary Cu/ZnO/TiO\(_2\) catalyst system is a potential candidate for this reaction and can be further enhanced by oxidative F\(_2\)-fluorination procedures.\(^{34}\) With a mild dilution treatment, the ZnO\(_\circ\) defect sites and the \(E_g\) for the RWGS reaction increase, while the \(E_g\) for MeOH production from CO\(_2\) hydrogenation is nearly unchanged, thus achieving optimized MeOH yield and selectivity. When compared with traditional Cu catalysts, many researchers have also engineered the d-band centers and the active center densities of Pd/Pt/Rh-based catalysts by incorporating non-noble metals to form an alloy and thus tuning their structures. Accordingly, an optimal Pd@Zn core–shell-structured catalyst was synthesized to further increase the kinetic barrier for CO formation, thus facilitating MeOH formation with the selectivity of 70% at relatively low pressure and temperature (2 MPa and 270 °C).\(^{35}\) Similarly, Diez-Ramirez et al. reported a Pd–Cu/Zn/SiC composite catalyst, and PdZn served as the active site for highly efficient MeOH production from CO\(_2\) hydrogenation (Figure 6a,b).\(^{36}\) Zeng’s group fabricated Pd\(_{74}\)Co octopods\(^{37}\) and Rh\(_{75}\)W\(_{25}\) nanosheets\(^{38}\) to catalyze CO\(_2\) hydrogenation with enhanced MeOH yields (Figure 6c–f). The alloying and specific morphology synergistically bring about the electronic effects of heterogeneous catalysts, which contribute to higher negative charge density and abundant active sites for enhanced CO\(_2\) activation and intermediate adsorption.

2.2.3. CO\(_2\) to CH\(_4\): CAMERE versus Formate Pathway

CO\(_2\) to CH\(_4\) (Sabatier reaction) is thermodynamically favorable, whereas the conversion undergoes an eight-electron process with high kinetic barriers. Therefore, the development of highly efficient catalysts is demanded to achieve satisfactory rates and selectivities.

\[
\text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}, \Delta H_{298K} = -252.9 \text{ kJ mol}^{-1}
\]

Many studies have sprung up for the Sabatier reaction based on the supported transition metal (e.g., Ni, Co, Fe, Ru, Pd, and Rh) catalytic systems. Meanwhile, metal oxides (e.g., SiO\(_2\), TiO\(_2\), Al\(_2\)O\(_3\), ZrO\(_2\), CeO\(_2\)) and carbon-based materials are the most commonly used supports, which provide high surface areas and heat-resistant properties. Notably, CO\(_2\) methanation involves two categories of mechanisms. 1) One involves CO\(_2\)-to-CO conversion followed by CO methanation, which proceeds via a Langmuir–Hinshelwood mechanism. In detail, the dissociation of CO\(_2\) into CO\(_\circ\) first happens through an RWGS reaction. Subsequently, methane can be generated by direct hydrogenation of CO\(_\circ\) intermediate or through a two-step pathway of dissociation of CO\(_\circ\) to the C\(^{\text{IV}}\) intermediate and further hydrogenation to methane. 2) The other one involves the direct hydrogenation of CO\(_2\) to CH\(_4\), and the formate species are suggested as the main reaction intermediates.\(^{39}\) Based on the proposed mechanisms, commercialized Ni-based materials were widely studied for Sabatier reaction at relatively high temperatures to overcome kinetic limitations. Mutschler et al. reported that Al\(_2\)O\(_3\)-supported Ni catalyst showed the maximum CH\(_4\) yield of 78% and selectivity of 98% at 623 K, accompanied with a small amount of gaseous CO (the highest CO yield of 18.2%).\(^{40}\) To further increase the CO\(_2\) conversion, Vita et al. synthesized Ni catalyst on gadolinium-doped ceria (Ni/GDC), which increased the amount of catalytic layer and thus achieved the highest CH\(_4\) productivity (10.7 L\(\text{CH}_4\)/h)\(^{-1}\)) at 400 °C during a 200 h continuous test.\(^{41}\) However, Ni-based catalysts show inactivation at a relatively high temperature as the interaction of Ni sites with CO intermediates could generate Ni carbonyl (Ni(CO)\(_4\)).
Therefore, the key is to develop efficient Ni-based catalysts and optimize reaction conditions, which ensure effective activation of the reaction system below 300 °C and finally achieve a high CH4 yield. For example, the automethanation phenomenon that happened on Ni/metal oxide (CeO2, ZrO2, Y2O3, or Al2O3) at room temperature and atmospheric pressure was reported to enhance the CO2-to-CH4 performance by purging a raw material gas containing oxygen into the reactor. The enhancement is mainly ascribed to the high thermal energy generated from H–O bond combustion under cofeeding with oxygen. Moreover, bulk LaNi5 alloy is well known for its hydrogen storage capability, which was also selected to realize improved activity for the Sabatier reaction. LaNi5 supported on γ-Al2O3 showed a high CO2 conversion (75%) and a superior CH4 selectivity (98%) at 1 atm and 300 °C (Figure 7a). From the DRIFT analysis (Figure 7b), the reaction went through an RWGS mechanism, which is described in detail as follows: H2 was first dissociated into *H on the surface of Ni sites and subsequently, CO2 was activated and dissociated on Ni sites. Then, the generated *CO rapidly adsorbed on LaOx decorations, and part of *CO was successively decomposed into *C and *O. Finally, the hydrogenation of *CO or *C was conducted to generate CH4.
the thermodynamic equilibrium, and thus the rapid reaction rate could be realized on Ru sites at a relatively low temperature without the requirement for an intermediate condensation step. Meanwhile, the metal loading of Ni is two orders of magnitude higher than that of Ru, indicating that Ru/Al2O3 is the preferable catalyst for small-scale CO2 methanation application. Sun et al. demonstrated that 5 wt% Ru/CeO2/MgO exhibited an efficient carbon capture and utilization (CCU) performance with a stable CO2 conversion (79%) and CH4 yield (3.36 mmol g\textsuperscript{-1} CO\textsubscript{2}) after 10-cycle CCU processes (Figure 7c,d).\[43\] Meanwhile, the introduction of oxygen vacancies into the Ru-oxide support interface is beneficial to improve the stability of the whole reaction system. The in situ DRIFT (Figure 7e) was further employed to explore the mechanism of the CO\textsubscript{2} methanation process under the synergistic effects of active Ru sites and oxygen vacancies. The proposed mechanism includes the following steps:

1) Adsorbed CO\textsubscript{2} molecules are activated by oxygen vacancies while CeO\textsubscript{2} support is oxidized, and H species are chemisorbed onto the active Ru sites. This step generates bidentate formate intermediate at the interface of metal support, which was then dissociated into metal carbonyl (Ru\textsubscript{2}CO) and O-H groups.
2) Ru\textsubscript{2}CO was hydrogenated by chemically adsorbed H species, which was finally converted into the CH\textsubscript{4} product and determined as the rate-determining step.

Figure 7. a) CO\textsubscript{2} conversion and CH\textsubscript{4} selectivity of La–Ni/γ-Al\textsubscript{2}O\textsubscript{3} in the Sabatier reaction. The inset in (a) shows the TEM image of the La–Ni/γ-Al\textsubscript{2}O\textsubscript{3} catalyst reduced in H\textsubscript{2} at 700 °C. b) The evolution of surface species as a function of time was analyzed by in situ DRIFT spectra of the La–Ni/γ-Al\textsubscript{2}O\textsubscript{3} catalyst after H\textsubscript{2} injection over preadsorbed CO\textsubscript{2} at 400 °C and 1 bar. Reproduced with permission under the terms of the CC-BY license.\[43\] Copyright 2016, The Authors. Published by MDPI. c) TEM image and d) CH\textsubscript{4} yield after 10-cycle CCU process of 5 wt% Ru/CeO\textsubscript{2}–MgO. e) In situ DRIFTS spectra during the CCU process of CeO\textsubscript{2}–MgO. Reproduced with permission.\[45\] Copyright 2020, Elsevier Ltd.
formation of CH₂O species by the consecutive hydrogenation of CO* intermediate were certainly enhanced. The above-mentioned steps could promote the cleavage of the C—O bond, which was regarded as the rate-determining step of the CO₂ methanation process.⁴⁶⁶

Cored et al.⁴⁷ synthesized a core–shell-structured Ru⁰@RuC catalyst by a facile hydrothermal method, which showed superior activity for CO₂-to-CH₄ conversion below 200 °C with 100% selectivity (Figure 8a,b). Analyzed by isotopic ¹³CO/¹²CO₂/H₂ experiments, the shell of RuC acted as the active site, which efficiently activates CO₂ and H₂, and finally CH₄ generation occurs via a direct CO₂ hydrogenation mechanism. Although noble metals (e.g., Ru, Rh, and Pd) have exhibited remarkable catalytic performance in the Sabatier reaction, the high cost and low storage have hindered their large-scale applications. Therefore, alloying noble metals with cheap metals (e.g., Fe, Co, Ni, Mn, Cu) can reduce the system cost and moreover, bring about the electronic effect and geometric effect for the enhanced catalytic activity. Herein, Zeng’s group demonstrated that face-centered tetragonal (fct)-PdFe intermetallic nanocrystals (NCs) presented high mass activity (5.3 mmol g⁻¹ h⁻¹) and stability for CO₂ methanation at 180 °C under 1 bar, which was 1.6, 3.3, and 5.3 times as high as that of Ru, Ni, and Pd (Figure 8c,d).⁴⁹ Evidenced by DRIFT measurements and DFT calculations, the metallic Fe sites were demonstrated to play a vital role in fct-PdFe intermetallic NCs, which facilitated the direct conversion of CO₂ into CO* intermediates, thus resulting in the enhanced hydrogenation of CO* into CH₄.

2.2.4. CO₂ to C₂+ Hydrocarbons: FT Synthesis versus Methanol-Mediated Pathway

CO₂ to hydrocarbons involves two different pathways, namely, the modified FT synthesis (FTS) and the methanol-mediated synthesis. The two pathways of thermocatalytic CO₂ hydrogenation can generate different products, which can be used as important industrial intermediates and high-value-added chemicals, etc. They are mainly alkanes (liquefied petroleum gas [C₃–C₄]₀ and gasoline [C₅–C₁₁]), alkenes (lower olefins [C₂–C₄=]), and aromatics.

1) The FTS pathway first generates CO from CO₂ hydrogenation via RWGS reaction and then obtains hydrocarbons through FTS (CO₂ + H₂ ↔ CO + H₂O; n CO + 2 m H₂ ↔ CₙH₂m + m H₂O). The first RWGS step in modified FTS is an endothermic reaction, which requires high temperatures to activate CO₂ molecules and accelerate reaction rates. However, FTS is an exothermic reaction, which indicates that lower temperatures could lead to fast hydrogenation of CO to multicarbon products.⁵⁰ Meanwhile, FTS goes through multiple steps, which involve reactants adsorption, chain initiation, growth, and termination, as well as product desorption for CO hydrogenation into carbonaceous compounds.⁵¹ Therefore, different catalysts and reaction conditions (temperatures, pressures, and CO₂/H₂ ratios) could significantly influence the CO₂ conversion rate and product yield as well as selectivity. As the traditional RWGS catalysts, Fe-based materials have been applied in the modified FTS process owing to their low cost and flexibility. In general, modification of these Fe-based catalysts is a prerequisite to realize enhanced CO₂
hydrogenation performance. The modification strategies can be categorized into the following four groups:

a) In situ structural transformation. Fe$_2$O$_3$ was reported to prefer the formation of light olefins (C$_2$+) rather than paraffin and suppresses the selectivity toward CH$_4$ and CO production at 623 K under a total pressure of 15 bar in CO$_2$ hydrogenation.$^{[52]}$ Analyzed by the X-ray diffraction (XRD) pattern and Mössbauer spectrum, the characteristic peak of iron carbides (Fe$_5$C$_2$) could be detected during CO$_2$ hydrogenation condition, which was obtained from the in situ transformation of Fe$_2$O$_3$. Importantly, Fe$_5$C$_2$ plays a vital role in the high selectivity of light olefin production and suppresses the high yield of CH$_4$ as Fe$_5$C$_2$ is an active phase to promote the FTS process and chain growth reaction. Accordingly, either the direct CO$_2$ methanation or CO-based FTS into CH$_4$ could be suppressed over the Fe$_2$O$_3$-based catalyst, and thus the selectivity of C$_2$–C$_4$ hydrocarbons increases to a value of 37% with the olefin to paraffin ratio of 2.7 at CO$_2$ conversion of 40%. Meanwhile, the selectivity of C$_5+$ hydrocarbons reaches 36%, while the values of CH$_4$ and CO were only 12% and 15%. This work provides in-depth sight into the fabrication of Fe-based catalysts toward CO$_2$ hydrogenation in terms of facilitating short-chain olefin formation and suppressing undesired C$_1$ products.

b) Alkali metals promotion. Alkali metals (e.g., Na and K) can act as promoters when introduced into Fe-based catalysts, which enhances the yield and selectivity for olefin production by accelerating CO dissociation and suppressing H$_2$ adsorption. In addition, the promoters significantly facilitate the formation of Fe carbides, which are well known as the active species for FTS reaction. Huang’s group synthesized a series of Fe-based catalysts with different amounts of Na dopants for CO$_2$ hydrogenation.$^{[53]}$ When Na content increases, CO$_2$ conversion rate and alkenes selectivity are optimized, and the highest values can be up to 36.8% and 64.3%, respectively, with the Na content of 1% (Figure 9a). With the assistance of the comprehensive investigations on the physical and chemical properties of xNa/Fe ($x$ indicates the weight percent of Na in wt%) catalysts, the promotion effects of Na dopant were determined to be the following key points. First, the interaction between catalysts and CO$_2$ molecules can be further enhanced in the presence of Na, which makes easier CO$_2$ activation. Second, Na facilitates the carbonization of Fe$_3$O$_4$ species in the presence of CO that is in situ generated from CO$_2$ hydrogenation, thus improving the formation and stability of Fe$_5$C$_2$ active species. The increasing amount of Fe$_5$C$_2$ species favors subsequent C–C coupling and carbon chain growth for heavier olefins (C$_2$–C$_4$ olefins and C$_5+$ hydrocarbons) production. Third, Na as a promoter could increase the CO dissociation and adsorption rate, considering that CO is an important reaction intermediate in the catalytic process of CO$_2$ hydrogenation into alkenes over Fe-based catalysts, which was also reported in a previous study.$^{[54]}$ Meanwhile, the Na promoter could inhibit the secondary hydrogenation of alkenes into alkanes as it can break the symmetry of

![Figure 9](image-url)
olefins and thus accelerate the desorption of olefins from the surface of the catalysts. Therefore, 1Na/Fe catalysts exhibited preferable heavy alkenes generation, while the selectivity toward methane production decreased to 7.2%. The possible reaction pathway is described as follows (Figure 9b): following a modified FTS process, CO2 and H2 molecules are first adsorbed and activated on the surface of the 1Na/Fe catalyst, and subsequently, the CO\textsuperscript{eq} species and H2O are generated via RWGS reaction. Then, the CO\textsuperscript{eq} species are dissociated and further hydrogenated into CH\textsubscript{4}, species and finally transformed into alkenes through a C–C coupling reaction. Potassium is also a popular promoter for Fe catalysts in CO2 hydrogenation, which facilitates CO2 capture via a well-known “potassium carbonate mechanism.” Moreover, K as an electron donor can accelerate the electron transfer from Fe-based catalysts to *CO intermediate, thus leading to higher selectivity toward olefins production via the FTS process. An active and stable Fe-based catalyst derived from the metal–organic framework (MOF) was reported by Ramirez et al. Potassium was found to be a great promoter, improving the space–time yields (STYS) toward C2–C4 olefin (33.6 mmol g\textsubscript{cat}\textsuperscript{−1} h\textsuperscript{−1}), which was significantly higher than other dopants (e.g., Cu, Mo, Li, Na, K, Mg, Ca, Zn, Ni, Co, Mn, Fe, Pt, and Rh) (Figure 9c,d).\textsuperscript{[55]} The possible reasons for the optimized promotion effects of the K lie in the fact that element K maintains the stability of Fe\textsubscript{3}O\textsubscript{4} and Fe\textsubscript{5}C\textsubscript{2}, which act as essential active species in CO2 hydrogenation. Followed by the proposed reaction pathway, CO2 was first adsorbed on Fe\textsubscript{3}O\textsubscript{4} active sites and converted into CO via the RWGS reaction and then underwent the hydrogenation process of CO via FTS on Fe\textsubscript{5}C\textsubscript{2} sites to produce light olefins (C2–C4). In addition, the K promoter can enhance the adsorption capability of CO2 and CO molecules while weakening H2 affinity, which causes a higher CO coverage and a lower H2 coverage on Fe-based reaction centers for a higher selectivity to olefins. Olefin selectivity on Fe\textsubscript{5}C\textsubscript{2} sites is closely associated with the secondary hydrogenation of olefins, which results in further chain growth and an overhydrogenation reaction. Therefore, during the FTS process, the K promoter strengthens the Fe–C bonds rather than the Fe–H bonds, contributing to a higher CO coverage on the surface of Fe-based active species. The increase of the CO/H2 ratio protects the catalytic sites from olefin read sorption and suppresses the formation of undesirable paraffin. Recently published studies demonstrate similar promoting effects of K element doping into Fe–Al–O spinel catalyst toward CO2 hydrogenation reaction.\textsuperscript{[56a,b]} To conclude, the K promoter imposes critical impacts on the catalyst phases (i.e., Fe oxides or carbides), chemical compositions, electronic states, and stability of the resulting Fe-based catalysts. Other K phases have also been introduced into Fe-based catalysts to activate CO2 and subsequently convert it into olefins through a tandem mechanism (RWGS + FTS pathways). For example, Fe\textsubscript{2}O\textsubscript{3}@K\textsubscript{2}O\textsubscript{3} and Fe\textsubscript{2}O\textsubscript{3}@K\textsubscript{2}O\textsubscript{3} reported by Gascon’s group yield similar productivity of olefins when compared with the commercial FTS catalysts.\textsuperscript{[57a,b]} c) Other metals promotion. Some non-noble metals, such as Cu, Zn, Mn, Co, and Ti, have also been introduced into Fe-based catalysts for CO2 hydrogenation. Cu promoter acted as a structural modifier that can increase Fe dispersion in the catalyst. Meanwhile, the incorporation of Cu into the Fe bulk lattice brought about optimized electronic effects, which facilitated CO2 activation and hydrogenation. Moreover, the olefin product distributions can be affected by alloying Fe with Cu. Noted that the addition of alkali metal further improves the RWGS and FTS tandem reactions as either a metallic or metal carbide active species can be maintained due to the interactions between Cu and K promoters. Hwang et al. reported that Fe–Cu–K catalyst showed high activity for liquid hydrocarbons production toward CO2 hydrogenation,\textsuperscript{[58]} which exhibited a C5\textsubscript{+} yield of 18.1%, much higher than that of Fe–K (12.8%) and Fe–Cu (23.8%) catalysts. The experimental results reveal that K is mainly responsible for CO formation; Cu–Fe species facilitates C–C coupling; Fe–Cu–K catalyst promotes the chain growth reactions. Higher alcohol synthesis (HAS) has been regarded as a popular pathway to obtain high-value C2\textsubscript{+} chemicals from CO2 hydrogenation. The catalysts applied in HAS process should keep a balance between alcohol formation (via dissociative CO activation) and olefin generation (via nondissociative CO activation) to achieve an optimal selectivity for C2\textsubscript{+}, alcohols. Noble palladium has been used to achieve high selectivity for ethanol production, but the high cost impedes its large-scale application.\textsuperscript{[59]} Xu et al. recently synthesized a CuFeZn catalyst with the addition of Cs promoter,\textsuperscript{[60]} which exhibited a satisfactory CO2 conversion efficiency (36.6%), C2–OH selectivity (19.8%), C2–OH STY (1.47 mmol g\textsubscript{cat}\textsuperscript{−1} h\textsuperscript{−1}), and C2–OH/ROH fraction (93.8%) (Figure 10a,b). The DRIFT and temperature-programmed surface reaction (TPSR) results indicated that the synergistic effects of Cu–ZnO and Cu–Fe–C active sites promoted a tandem reaction for the C2–OH alcohol synthesis. In detail, RWGS reaction first proceeded on Cu–ZnO sites to form CO\textsuperscript{eq} intermediates, which were hydrogenated into C2–OH via surface alkyl intermediates over Cu–Fe–C3 sites, therefore simultaneously suppressing the direct CO2 hydrogenation into methanol via formate intermediates (Figure 10c). Meanwhile, higher CO2-to-alcohol conversion was achieved with the addition of 3 wt% Cs promoter as Cs addition weakens hydrogenation ability, similar to the role of K promoter played in CO2 hydrogenation. Other transition metals like Mn and Co were also incorporated into Fe-based catalysts to obtain high CO2 conversion and optimal selectivity for light olefins production.\textsuperscript{[61a,b]} These studies prove that the Mn and Co can be preferable alternatives for enhanced CO2 adsorption and activation while hindering the secondary hydrogenation to reach high olefin/paraffin (O/P) ratios. Compared with the bulk morphology of Fe, element Ti was introduced as a structural promoter into the Fe-based catalyst to form a Fe–Ti–O-layered oxide material, which results in higher dispersion of Fe active sites and more stable phrase structure for highly selective CO2-to-olefins conversion.\textsuperscript{[62]} d) Supports optimization. Different supports have been applied to optimize the metal dispersity, size, and metal–support interactions that resulted from their unique physicochemical properties. Metal oxides are supposed to be ideal candidates used to applied to optimize the metal dispersity, size, and metal–support interactions that resulted from their unique physicochemical properties. Metal oxides are supposed to be ideal candidates used to
isomerization of hydrocarbons. Accordingly, Wei et al. combined Na–Fe₃O₄ catalyst with an HZSM–5 zeolite into a multifunctional catalyst,[64] which hydrogenated CO₂ into heavy hydrocarbons (C₅–C₁₁) with a selectivity of 78% among all hydrocarbon products, whereas efficiently decreases methane yield. Meanwhile, the as-synthesized catalyst showed superior stability during a 1000 h test, which could be comparable with the industrially applied catalysts for CO₂ conversion into liquid fuels. The proposed pathways of Na–Fe₃O₄/zeolite-multifunctional catalyst for CO₂-to-liquid fuels conversion are described as follows: CO₂ molecules are first activated and reduced to CO after hydrogenation via RWGS process on Fe₃O₄ active species and then the hydrogenation of CO to olefins on in situ-formed Fe₅C₂ sites via FTS reaction. Subsequently, the olefin intermediates could diffuse to zeolite acid sites and process a series of oligomerization/isomerization/aromatization reaction steps, and thus the heavy hydrocarbons, especially gasoline-range isoparaffins and aromatics, are formed after desorption from zeolite pores. In addition, a variety of carbon-based materials such as carbon nanotubes, porous carbons, and carbon nanofibers have also been selected as promising supports due to their thermal conductivity, high surface area, electron enriched surface, and high stability. Herein, single-walled carbon nanotubes[65] and mesoporous carbon[66a,b] are synthesized as supports for Fe-based materials, which realize enhanced CO₂ conversion efficiency, optimized selectivity of light olefins (C₂–C₄), and O/P ratio at catalytically active Fe carbide sites through a tandem reaction combining RWGS with FTS processes.

Figure 10. a) CO₂ conversion (yellow open squares) and selectivities of alcohol, olefin, C₂, alkane, CH₄, and CO in all carbon products. b) Distribution of alcohols in STY and weight fraction of C₂,OH/ROH (brown solid circles) over x%Cs–CuFeZn catalysts. c) The possible pathway of Cs–CuFeZn in CO₂ hydrogenation. Reproduced with permission.[60] Copyright 2020, American Chemical Society.
2) The methanol-mediated synthesis pathway for CO₂-to-hydrocarbons conversion also involves two steps, namely, CO₂ is first hydrogenated into MeOH and then reduced into multicomponent compounds. In recent five years, many studies focus on the MeOH-to-olefin conversion, which was thermodynamically initiated at high temperatures (>300 °C). However, CO₂-to-MeOH conversion is an exothermic step that is not favored at such high temperatures, and CO is produced as a byproduct through an endothermic RWGS process. Therefore, zeolite as a solid acid catalyst has been applied for C–C coupling (≥350 °C) and converts MeOH into olefins, which effectively suppresses CO production. Especially, the SAPO-34 and ZSM-5 zeolites are commonly used as active components for methanol conversion to olefin processes at a level of industrialization. Combining ZnO–ZrO₂, CuO–ZnO–ZrO₂, In₂O₃–ZrO₂, ZnGa₂O₄, or ZnO–Y₂O₃ with SAPO-34 zeolite as composite catalysts have been applied to CO₂ hydrogenation. When referred to SAPO-34, the generated MeOH intermediate is first converted into active hydrocarbon pool species (CH₃OH) inside the channels. Then, MeOH reacts with (CH₃)ₓ species to produce light olefins (C₂–C₄) and is further converted into higher olefins, alkanes, and aromatic through condensation, alkylation, and cyclization processes.

Li’s group reported a ZnO–ZrO₂/SAPO tandem catalyst that successfully converted CO₂ to light olefins (C₂–C₄) with high selectivity of 80–90% among hydrocarbon products (Figure 11a,b). CO₂ hydrogenation proceeded on the surface of ZnO–ZrO₂ to generate CH₃OH intermediates (precursors of MeOH), and subsequently lower olefins were produced on the SAPO zeolite (Figure 11c). To improve the catalytic activity of CO₂-to-MeOH conversion of Zn–Zr composites, Cu–ZnZr catalyst with core–shell structure was synthesized by Chen et al. Under a low concentration of MeOH intermediate, the reduced contact interface and hydrogenation ability on the reaction centers successfully suppress CH₄ production and achieve a high olefin selectivity of 72% at 400 °C and 2 MPa total pressure. The hybrid catalyst of In₂O₃–ZrO₂/SAPO-34 was also found to exhibit high selectivity of C₂–C₄ olefins with an ideal CO₂ conversion efficiency at 400 °C via a direct tandem catalysis process by combining a CO₂-to-MeOH catalyst (In₂O₃–ZrO₂) with a methanol-to-olefins catalyst (SAPO-34). In other words, methanol could be generated at the active sites (oxygen vacancies) of In₂O₃–ZrO₂ in the first step, which subsequently went through the SAPO-34 channels and was converted into light olefins automatically. The vital roles of the oxygen vacancies were also confirmed on ZnGa₂O₄ catalyst toward the direct conversion of CO₂ to C₂–C₄ olefins.

Analysed from in situ infrared spectroscopic tests, the oxygen vacancies effectively activated CO₂ molecules, and simultaneously –Ga–O– and –Zn–O– pairs dissociated H₂ into H species. Then methoxide species (CH₃O⁻) were formed upon prolonging the time, which were further hydrogenated into MeOH intermediates. Finally, MeOH diffused into the channels of SAPO-34 and thus selectively generated light olefins. As a bifunctional oxide–zeolite catalyst could initiate CO₂-to-MeOH and C–C coupling on two different active sites, ZnO–Y₂O₃ incorporated SAPO-34 zeolite was reported as another alternative to realize a high selectivity of light olefins production (83.9%) with low CH₄ selectivity (1.8%) toward CO₂-to-hydrocarbons. ZSM-5 zeolites have been applied together with other metal oxides to enhance the selectivity of valuable C₅–C₁₄ fuels in CO₂ hydrogenation. The involved mechanism was the concept of the dual cycles: olefins-based cycle and aromatics-based cycle. Methanol intermediates were first converted into olefinic species, and then propene and higher alkenes were obtained from alkenes methylation and cracking in the olefins-based cycle. Meanwhile, higher alkenes could be converted into toluene by oligomerization and cyclization. Furthermore, in the aromatics-based cycle, ethene was generated from methylation of toluene and side-chain elimination. Moreover, aromatics were simultaneously generated by successive oligomerization, cyclization, and dehydrogenation processes. Accordingly, an active catalyst composed of ZnO–ZrO₂ aerogel and H-ZSM-5 zeolite (ZnO–ZrO₂/H-ZSM-5) realized CO₂ conversion of 16% with the aromatics selectivity of 76%, while the selectivity of CH₄ was less than 1% at 340 °C and 40 bars (Figure 11d,e). The MeOH intermediate was first generated over the oxygen vacancies on the surface of ZnO–ZrO₂, and then the aromatic hydrocarbons were generated from MeOH species in H-ZSM-5 via the above mechanisms (Figure 11f). Similarly, the ZnCrO₃–ZnZSM-5 compound was used in CO₂-to-hydrocarbons conversion, which resulted in the highest aromatics selectivity of 81.1% in C₅+ hydrocarbons with 19.9% CO₂ conversion at 320 °C.

3. Photocatalysis

3.1. Motivation and Principles

Photocatalytic CO₂ reduction (PCR), the so-called artificial photosynthesis, takes advantage of solar energy to activate CO₂ molecules and subsequently convert them into different products such as HCOOH, CO, CH₄, HCHO, or CH₃OH over semiconductors (Figure 12a). PCR is a promising technology that can convert CO₂ waste into solar fuels, thus realizing the recycling of renewable carbon fuels and retaining carbon neutrality without secondary pollution. Though much efforts have been made to optimize CO₂ photoreduction to fuels under solar light, the overall photoconversion efficiencies are very limited for practical application and there is a lack of a standard for solar-driven CO₂ conversion efficiency that needs to be achieved for practicality. Therefore, if a CO₂-to-fuel photoconversion technology is ever to become a reality, a significant advance is required. Recently, a rationally designed Cu–Pt/TiO₂ photocatalyst reported by Sorcar et al. could achieve a satisfying photoconversion efficiency of 1.0% with an apparent quantum yield (AQY) of 86% over 6 h under artificial sunlight (AM1.5), which successfully converted CO₂ and H₂O to a fuel compatible with our current energy infrastructure. Nevertheless, the reaction mechanisms are required to be thoroughly explored, which can contribute to the optimization of the photocatalysts and photocatalytic processes.

In general, the PCR process involves four steps: 1) the formation of excitons within semiconductors upon the illumination with efficient energy larger than the bandgaps of the semiconductor photocatalysts; 2) excitons’ dissociation into hot electrons to the conduction band (CB) and leaving holes in the valence band (VB) driven by the built-in electric field; 3) charge carriers...
migration to the surface active sites; and 4) transformation of CO₂ into carbonaceous compounds by the photogenerated electrons when the location of CB is more negative than the redox potentials of CO₂ reduction half reactions. Meanwhile, the holes in the VB of semiconductors should contribute to the oxidation of H₂O to O₂ when the VB edge is more positive than the redox potential of H₂O/O₂. The H₂O oxidation process can be replaced by organic upgradation to value-added chemicals with a matching oxidation potential so that the CO₂ reduction process can be integrated with the organic oxidations. Notably, the photocatalysts are the keys to the successful transformations and should be carefully designed as their bandgaps should be suitable to not only satisfy the large overpotentials of the abovementioned redox reactions but also broaden the utilization of solar energy. Moreover, the electronic and geometric structure of the photocatalyst should be optimized to suppress the recombination of e⁻/h⁺ pairs, aiming at improving the lifetimes of photogenerated carriers and quantum efficiency. Furthermore, the
modification and reconstruction of the surface structure of the employed photocatalysts to increase the number of active sites are vital to the adsorption and activation of CO2 molecules, which can facilitate the electrons transfer from photocatalysts to CO2. In addition, the introduction of proper cocatalysts onto photocatalysts can provide an optimized interface to accelerate the photocatalytic electron transfer rate and accumulate a large number of electrons for CO2 reduction reaction (CO2RR), which can effectively prolong the lifetime of e−/h+ pairs and improve the overall quantum efficiency. Finally, the binding energies of reaction intermediates should be optimized to facilitate the desorption of intermediate species, thus avoiding the “poison” phenomenon of photocatalysts and effectively terminating the PCR reaction for the formation of high-value-added carbonaceous products. The extensively studied PCR systems can be divided into the following five categories (Figure 12b): one-step excitation semiconductor system, one-step excitation photosensitized semiconductor system, two-step excitation heterojunction system, two-step excitation direct Z-scheme system, and two-step excitation indirect Z-scheme system.

3.2. Plausible Systems for CO2 Conversion

Up to now, numerous works associated with photocatalysts have been reported for CO2 reduction, such as metal oxides (e.g., TiO2,[78] Ga2O3,[79] Co3O4,[80]), metal chalcogenides (Cu1SnS4),[81] metal halides (Bi12O17Cl2),[82] bimetallic oxides (e.g., NiCo2O4,[83] CoTiO3),[84] bimetallic layered double hydroxides (LDHs) (e.g., Mg, Co, Ni, Cu, Cu, and Zn-based LDH),[85a–c] and metal-free carbon-based materials (e.g., graphene oxide, g-C3N4).[86a,b] The catalytic activities of these photocatalysts can be optimized by the modulation of their electronic and/or geometric structures, including the design of morphology, defect, and oxygen vacancies. The CB of photocatalyst should satisfy the redox potential of CO2 half reaction and thus thermodynamically drive CO2 conversion into carbonaceous compounds.
However, their wide bandgaps and rapid recombination of photoinduced electron/hole pairs restrict their utilization of solar light and minimize the lifetime of charge carriers, as well as the photoactivity, stability, and AQY of PCR.

3.2.1. One-Step Excitation Semiconductor

One-step excitation semiconductor system is a commonly employed candidate to drive PCR with the assistance of a cocatalyst (e.g., Pd, Pt, Ag, Au, Cu, and Ni). Once the semiconductor photocatalyst absorbs solar light, the photoinduced electrons could thermodynamically flux to the cocatalyst as the Fermi level of the cocatalysts situates below the CB of semiconductor, which acts as dual roles of electron “accumulation pool” and active sites for CO₂ reduction. The loading and structural optimization of cocatalysts could enrich the number and intrinsic performance of active sites, thus facilitating the activity and selectivity of PCR. For instance, Bai and co-workers hybridized TiO₂ nanosheets with Pd cocatalyst to investigate the performance of the hybrid structures toward CO₂-to-fuel conversion.¹⁸⁷ Note that the Pd cocatalyst with a small nanosheet structure provides abundant edge sites for the enhancement of charge kinetics, CO, and CH₄ formation rates toward CO₂RR (Figure 13a–c), which adequately interpreted the edge-dependent photocatalytic performance. Meanwhile, Pd nanosheets could attract photoinduced electrons from TiO₂ to prolong the lifetime of electron–hole pairs, which effectively enhanced the stability of the overall catalytic system. Furthermore, the plasmonic effect of the Pd metal induced by visible light could generate “hot” electrons, which were then injected into the CB of TiO₂ to improve the light absorption ability of TiO₂, and thus realized the efficient CO₂ conversion under visible light irradiation. Yu’s group deposited Pd cocatalyst onto the surface of graphitic carbon nitride (g-C₃N₄) and explored the facet effect of Pd toward PCR performance.¹⁸⁸ The Pd nanoparticles broaden the light absorption range of bare g-C₃N₄, which is mainly attributed to a localized photothermal effect of Pd. Meanwhile, the interface between Pd with g-C₃N₄ could form Schottky barriers, which effectively separated photogenerated carriers to facilitate the separation of electrons and holes. The electrons generated from the g-C₃N₄ surface could flow and accumulate on the surface of Pd nanoparticles, which were responsible for the long-term activity and selectivity of PCR.

Figure 13. a) Schematic illustration of TiO₂–Pd nanosheet (NSs)–S. Time-dependent b) CO and c) CH₄ formations on TiO₂–Pd NSs–S in PCR. Reproduced with permission.¹⁸⁷ Copyright 2017, The Royal Society of Chemistry. d) HRTEM image of 0.5%Pt–WO₃. The e) CO and f) CH₄ production versus reaction time over 0.5%Pt–WO₃ photocatalyst. Reproduced with permission.¹⁹⁰ Copyright 2019, Elsevier B.V. g) The adsorption and desorption thermodynamics of CH₃OH@Cu/CN. h) The schematic illustration of CH₃OH@Cu/CN toward CO₂-to-CH₄ conversion in PCR. Reproduced with permission.¹⁹³ Copyright 2019, The Royal Society of Chemistry.
CO₂ hydrogenation and the formation of CH₃OH. Moreover, the experimental results and DFT calculations verified that the optimized ratio of (111)/(100) facets of Pd could facilitate the interfacial charge carrier mobility, CO₂ adsorption ability, and CH₃OH desorption.

Metallic Pt has also been employed as a cocatalyst to improve the photoactivity of semiconductors in CO₂RR. For example, Wang and co-workers decorated Pt nanoparticles onto the surface of SiC nanosheets to study the synergistic effects for the enhancement of activity and selectivity in CO₂-to-CH₄ conversion. The Pt nanoparticles as the cocatalysts could attract the photogenerated electrons from SiC, which increased the local electron densities around the active sites for the 8-electron CH₄ formation process. It should be mentioned that the generated CO intermediates could be well stabilized on Pt and were further reduced to CH₄ by the accumulated electrons on Pt “island.” Similarly, Liu’s group introduced different amounts of Pt on hexagonal WO₃ to enhance the mobility and lifetime of the photo-generated carriers. Moreover, Pt adjusted CO adsorption ability and electronic localization, thus realizing highly selective CO and CH₄ formation in the PCR process (Figure 13d–f).

TiO₂ is the most studied material in PCR during the past decades, and the incorporation of metals such as Ag and Au has been demonstrated to be an effective approach to improve the catalytic performance of TiO₂. The particle sizes of the cocatalysts significantly influence the selectivity for CO₂ conversion. Hammad et al. reported Ag-loaded TiO₂ catalysts with different sizes of Ag nanoparticles via a photodeposition method in different atmospheres. The study found that smaller Ag nanoparticles could be prepared on the surface of TiO₂ in the absence of O₂, and showed higher selectivity in CO₂-to-CO conversion. The main reason for the enhanced PCR lies in the fact that smaller Ag nanoparticles could efficiently collect abundant photoexcited electrons from the CB of TiO₂, which could accelerate CO₂ activation and CO desorption. Meanwhile, localized surface plasmon resonance (LSPR) of Ag nanoparticles broadened the photoabsorption range, which enhanced the utilization of solar light and photoactivity of the overall catalytic system. Au is also an ideal cocatalyst, which imposes LSPR effects to broaden the sunlight absorption range to visible light regions. Moreover, the hot electrons generated from Au nanoparticles activated the adjacent electrons through energy transfer and increased local temperature, which could improve the catalytic kinetics and efficiency of PCR. Furthermore, the Schottky junction between Au and semiconductors promoted the migration of electrons from semiconductors to Au nanoparticles, which facilitated the separation of the photo-induced carriers, thus achieving long-term catalytic stability.

Except for noble metals, some non-noble metals such as Cu and Ni have also demonstrated their effectiveness as cocatalysts for the selective CO₂RR in photocatalytic systems. Li et al. deposited Cu nanoparticles on CN, which realized high selectivity for CH₄ formation. Demonstrated by the kinetics and thermodynamics results, the precisely tailored Cu/CN interfaces could establish binary electron transfer channels, which contributed to the CH₃OH intermediate activation and further hydrogenation reaction for the final CH₄ product formation (Figure 13g,h). Xu and co-workers prepared Ni@graphitic carbon (GC) catalyst composed of Ni nanoparticles on the surface of a few-layered GC. The presence of Ni cocatalyst could bind to GC via Ni–C bonds, which efficiently accelerated the mobility and separation of photoinduced carriers, and CO₂ adsorption, which resulted in high efficiency in PCR.

In addition, other materials like alloys, metal oxides, inorganic quantum dots (QDs)/nanosheets, etc. Metal complexes for PCR were mainly based on bipyridine, and porphyrin units, among which the Ru—bipyridine complex has been the most popular choice to be used as the photosensitizer due to its good stability and suitable energy level. For example, TiO₂(CO₃)₂(Al₂O₃) α-Fe₂O₃ NiAl-LDH (NiAl-LDH₄) and Co₃P have been used as the catalysts with the combination of Ru(bpy)₂Cl₂·6H₂O as a photosensitizer to form a hybrid photocatalyst system. The photosensitizers first adsorb incident light to generate electrons, which transfer from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) of photosensitizers. Subsequently, the electrons flow to the CB of semiconductors and perform a highly selective CO₂-to-fuel conversion (e.g., formic acid, CO, and CH₄). Ir(bpy) is another commonly used photosensitizer that has a strong visible light absorption band, which participates in the PCR catalyzed by a Ru-based complex to realize CO₂-to-formate conversion. Non-noble metal-based photosensitizers have also attracted some attention for PCR. For example, Kang and co-workers prepared a series of Zn–porphyrins anchored on the TiO₂ surface to achieve a lower energy sensitization and increased catalytic stability. The hybrid catalyst exhibited a high turnover number (TON) of ≈800 and a long lifetime of 90 h under red light irradiation (∼550 nm) for CO₂-to-CO conversion (Figure 14a,b). The introduction of functional groups (e.g., acetylene, –COOH) to Zn–porphyrins could improve the energy-harvesting ability, photoinduced electron mobility, and binding capability at TiO₂. Recently, heteroleptic diamine–diphosphine Cu(C(dpbb)) complexes were regarded as popular choices to explore their photosensitizing abilities in the PCR system. Tsuobumura and co-workers found that the optimized performance would be achieved when the length of the carbon chains between the two phosphorus atoms in the diphosphine ligands is extended. Using Re(bpy) as a catalyst and Cu(dpbb) as a photosensitizer, a robust hybrid system was designed to realize visible light-driven CO₂ reduction to CO. The Co–quaterpyridine...
molecule complex has also been regarded as a highly efficient and selective homogeneous sensitizer. Accordingly, Robert’s group designed a novel molecule-material hybrid by covalently immobilizing Coqpy-Ph-COOH onto mpg-C$_3$N$_4$ through an amide linkage,\[109\] which exhibited high selectivity for CO production (98%) and long-term stability (no degradation after 4 days) upon a solar simulator. Finally, the same group reported a Co$_2$/C$_0$ quaterpyridine complex, which has been covalently attached to graphene surface by carboxylic acid groups.\[110\] The as-prepared catalyst was proved to be a highly active material toward visible light-driven CO$_2$ conversion in acetonitrile, which showed extraordinary stability (>200 h irradiation) and high selectivity of carbonaceous products (>97%). Importantly, the product selectivity could be completely controlled by varying experimental conditions: CO as the only product was achieved in phenol or trifluoroethanol (a weak acid), while formate was obtained in a mixed solution of acetonitrile and triethanolamine.

Organic dyes are another class of widely employed photosensitizers. Robert and co-workers reported that purpurin served as a simple organic photosensitizer to be used in PCR together with a molecular Fe(II) catalyst,\[111\] which realized highly selective CO$_2$-to-CO conversion (FE$_{CO} = 95\%$) under visible light illumination (>200 h irradiation) and high selectivity of carbonaceous products (>97%). Importantly, the product selectivity could be completely controlled by varying experimental conditions: CO as the only product was achieved in phenol or trifluoroethanol (a weak acid), while formate was obtained in a mixed solution of acetonitrile and triethanolamine.

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could transfer from the CB of IL–nCO₂ to the CB of TiO₂ and finally launch the visible light-driven CO₂-to-CH₄ conversion over the TiO₂ surface.

Employing inorganic materials as photosensitzers is beneficial to experimental studies and mechanism exploration. As low-cost, stable, and nontoxic light harvesters, carbon dots can be coupled with other photocatalysts, thus exhibiting a wide spectral response in PCR. Li’s group proposed carbon dots-hybridized MOF photocatalyst,[114] which exhibited enhanced activity than the pristine MOFs in CO₂ reduction. Carbon dots serve as excellent photosensitzers for a highly efficient PCR system under long-wavelength light irradiation, which can be ascribed to the polyaromatic units and functional groups with strong π–π* and n–π* transitions of carbon dots. Mn-doped semiconductor QDs reported by Son et al. showed higher photostability and broadened the absorption range of photosensitization,[115] thus activating the Ni(cyclam)-based molecular catalyst for enhanced activity and highly selective CO₂-to-CO conversion. This can be explained by the reason that the energetic hot electrons induced by Mn-doped QDs enable the long-range interfacial electron transfer in “nonlinked” QDs/molecular catalyst hybrids, which contributed to six times higher production amounts in CO₂-to-CO conversion than the pristine Ni(cyclam)²⁺ system. In addition, mesoporous graphitic CN (mpg-C₃N₄) is also an ideal redox photosensitizer used in PCR due to its strong visible light response and high stability under sunlight illumination in various solvents, especially H₂O. For example, Cao and co-workers fabricated a polymeric CN catalyst on the surface of carbon paper via a chemical vapor deposition method.[116] The addition of phosphate realized a high selectivity of 93.8% toward CO₂ photoreduction to carbonaceous chemicals with an AQY of 0.4%. This study opened a new era for designing efficient photocatalysts of CO₂ reduction in aqueous solution, which also found that phosphate plays a key role in the CO₂ conversion process. Robert et al. reported a hybrid photocatalytic system containing Fe–complex catalyst and mpg-C₃N₄ photosensitizer for the first time,[117] which exhibited a high FEₐₐ value of 97% and a TON of 155 with an AQY of ≈4.2% (Figure 14c–e). The mpg-C₃N₄ possessed enough negative CB minimum (~1.35 V vs calomel electrode (SCE)), which could reduce the Fe⁶⁺(qpy)(CO₂)²⁻ to achieve an enhanced CO formation under visible light irradiation. Halide perovskite colloidal NCs are also promising alternatives to replace the organic photosensitzers, which possess many advantages such as low nonradiative recombination rates, as well as tunable chemical composition and structures. Accordingly, Chen et al. prepared inorganic ligand-capped CsPbBr₃ NCs as visible light-harvesting photosensitzers, which exhibited low-cost, rich active sites, and a high molar extinction coefficient.[118] Furthermore, the [Ni(terpy)₂]²⁺ was immobilized on the surface CsPbBr₃ NCs forming a hybrid catalyst, which showed a high yield of 1724 μmol g⁻¹ for CO/CH₄ production in CO₂ photoreduction. The CsPbBr₃ NC photosensitizer offered abundant surface sites to tightly immobilize Ni-based complexes. Meanwhile, CsPbBr₃ NCs can broaden the light absorption range and provide a large number of photoinduced electrons to Ni-based catalytic sites for the PCR system. Some other metal-based compounds have also been applied as photosensitzers due to their strong light responses. For example, Bian and co-workers reported the use of BiₓWO₆ particles as photosensitzers and Mn complexes as the catalyst for the highly selective CO production toward PCR.[119] He’s group proposed a promising strategy to achieve an efficient, selective, and stable PCR system,[120] in which ZnₓCd₁₋ₓS was used as the photosensitizer to couple with Fe-based molecular catalyst. The results showed that ZnₓCd₁₋ₓS facilitated charge separation and mobility, as well as visible light response. This group further combined BiₓS₃ with Cds as a hybrid photosensitizer in another work,[121] which not only exhibited enhanced visible light absorption due to its narrow bandgap but also improved the photoinduced electron transport efficiency between the Z-scheme Cds/BiₓS₃ photosensitizer and the Fe-based catalytic center. Thereby, the system achieved improved CO yield in CO₂ photoreduction. In summary, the one-step excitation (photosensitized) semiconductor system has commonly been conducted in organic solutions, which hardly exhibits satisfying photocatalytic performance, as H₂O is essential for the significant promotion of catalytic activity and stability. Moreover, the use of organic solvents and sacrificial reagents hinders its practical application due to its deficient environmental protection, and thus exploring the hybrid systems with the absence of organic solvent conditions and sacrificial reagents will be more promising in the PCR field.

3.2.3. Two-Step Excitation Heterojunction

Two-step excitation heterojunction system has been regarded as a coupled system of two semiconductors used in photocatalytic reactions, where semiconductors are photoexcited to generate electrons and holes on their VB and CB, respectively, and then, the photoinduced carriers would flow within the hybrid materials depending on the relative energy potentials of CBs and VBs. In terms of the band structures of the coupled semiconductors, the heterojunction system has commonly been divided into three categories: straddling gap (type I), staggered gap (type II), and broken gap (type III) (Figure 15).[122] In comparison, type II heterojunctions are considered the most popular choice to facilitate the separation of electron/hole pairs: the electrons would transfer to the semiconductors with a more positive CB position, while the holes flowed to the semiconductors with a more negative VB position. Accordingly, the flow directions of electrons and holes are opposite, which can significantly suppress the recombination of the photogenerated charge carriers and enhance the efficiency of the PCR system. Meanwhile, the different semiconducting components employed in heterojunctions can broaden the light absorption range due to their appropriate band structures. TiO₂, carbon, g-C₃N₄, and other oxides/chalcogenides/carbonates/oxysalts-based materials are the most commonly applied components in type II heterostructures for highly efficient PCR. Wang and co-workers designed a paragenetic anatase/rutile TiO₂ heterostructure by a facile phase transformation method.[123] The two-phase TiO₂ heterojunction facilitated CO₂ absorption capacity and photoinduced carrier mobility and then activated the redox reaction of CO₂/CO₂⁻, thus realizing a better selectivity for CO production when compared with P25. In addition, some low-cost materials like metal oxides or sulfides with visible light response have been applied to realize efficient charge transfer and enhanced solar energy utilization of TiO₂. For example, a well-connected TiO₂/ZnO heterojunction achieved
an improved photocatalytic yield of CO2 reduction to CH4 (2.56 μmol g⁻¹ h⁻¹) than pure TiO2 (0.55 μmol g⁻¹ h⁻¹). The optimal performance could be attributed to the rapid photoexcited carrier mobility and slow recombination of electron/hole pairs. Although the as-prepared heterojunctions could convert CO2 into solar fuels, the light absorption regions still required to be broadened. Accordingly, WO3-x nanowires were prepared onto the surface of mesoporous TiO2 by Li’s group, leading to a strong SPR which extended the light response range of the whole catalytic system to visible and near-infrared light. Hence, the TiO2/WO3-x heterojunctions exhibited a high production rate of CH4 (16.3 μmol g⁻¹ h⁻¹) during PCR than the pristine TiO2 (3.5 μmol g⁻¹ h⁻¹) and WO3-x (8.0 μmol g⁻¹ h⁻¹) (Figure 16a,b). Within the heterojunction, TiO2 provides continuous photogenerated electron injection, which plays an important role in the stable SPR of WO3-x. Subsequently, the plasmonic hot electrons induced from WO3-x nanowires could efficiently suppress hydrogen evolution reaction (HER) under UV–vis light irradiation, thus resulting in CH4 formation with impressive efficiency and high selectivity (Figure 16c). Meanwhile, TiO2 was also combined with CaTiO3 or Cu2ZnSnS4 to fabricate heterostructure composite, which possessed an intimate contact at the interface due to their appropriate band structures and matching crystal structures. The hybrids not only enhanced the surface basicity to provide abundant active sites for improved CO2 absorption and activation but also improved the lifetime of photogenerated carriers to achieve an efficient and selective CO2 conversion to gaseous hydrocarbons (e.g., CO, CH4) than pristine TiO2. In addition, Lee and co-workers prepared a reduced form of black TiO2 to widen the absorption region via H2-mediated reduction step. A disordered structure of TiO2 was developed with a blueshift of the XPS peak of Ti–O, which was caused by the occupation of the oxygen vacancies by electrons. Moreover, g-C3N4 was introduced and wrapped with black TiO2 to form a meta-heterostructure. Engineering 2D/2D heterojunction photocatalysts provided a high interfacial contact area and high density of active sites, which contributed optimized physicochemical properties (e.g., charge carrier dynamics) and thus facilitated the employment of solar energy as a sustainable energy source. Accordingly, the resulting g-C3N4-black TiO2 showed increased light absorption at 470 nm. Moreover, the CBs and VBs of the heterojunction processed proper positions for the redox reactions of CO2/CH4 and H2O/O2, respectively, thus reaching improved yields and stability for both CO and CH4 productions than the pure black TiO2.

C3N4-based heterojunctions are another class of popular alternatives used in highly efficient PCR, which facilitates photocatalytic efficiency by enhancing light absorption, charge separation, and mass transport. Li and co-workers designed 2D g-C3N4 nanosheets which acted as a soft template to immobilize Co3O4 platelets through a facile method. The hybrids achieved an enhanced photocatalytic performance which was 13.5- and 2.6-fold higher than that of pure 2D g-C3N4 and Co3O4. The synergistic effects of 2D g-C3N4 and Co3O4 not only facilitate the photoinduced carrier transportation due to the large specific surface area of 2D g-C3N4, but also contribute to the accumulation of electrons onto the surface of g-C3N4 from the CB of Co3O4 for the absorption and reduction of CO2 intermediate, thus improving photocatalytic properties (activity, selectivity, and stability) of the whole system under UV–vis light irradiation. As a visible light transducer, CdS shows a wide light response range and has been frequently selected as a photoharvester in photo-redox reactions. For example, Wang and coworkers improved the PCR activity of boron-doped bulk CN (BCN) semiconductors by surface engineering with CdS, which exhibited 10 times higher CO2 reduction activity than that of BCN under visible light illumination (Figure 16d,e). Due to the inner electric field of CdS/BCN heterojunctions, CdS as sensitization material could first absorb visible light and then transferred the photoinduced electrons to the CB of BCN and finally activated and reduced CO2 molecules to CO. The improved activity is mainly due to the improved visible light absorption and facilitated transport/separation of electron/hole pairs (Figure 16f). Interestingly, the ternary metal sulfides have also been used with g-C3N4 to fabricate type-II heterojunction for CO2 photoreduction. For example, CdIn2S4 or Zn0.2Cd0.8S was prepared and combined with g-C3N4, which enhanced the CO2 adsorption ability, charge mobility, and electron/hole pair separation efficiency and thus achieved higher photocatalytic activity and stability for the CO2-to-CH3OH conversion under visible light than pristine g-C3N4. In addition, with the appropriate band structures, C3N4 could connect with Bi4NbOCl, LaPO4, BiFeWO6, NiAl-LDH, Mexene (e.g., Ti3AlC2 or MOFs (e.g., Zr-based MOF, NH2-MIL-101(Fe)), The charge transfer and separation phenomenon can be observed in these type-II heterostructures.
through a two-step excitation process. In detail, the photogenerated electrons could escape from the CB of C$_3$N$_4$ under visible light illumination and then be transferred to the CBs of these semiconductors, while the holes induced from the VBs of these semiconductors could flow to the VB of C$_3$N$_4$, thereby launching the CO$_2$ reduction and water oxidation/sacrificial reagents on the CB of the additional semiconductor and VB of C$_3$N$_4$, respectively. Thanks to the synergistic effects between C$_3$N$_4$ and these semiconductors, the separation efficiency of electron/hole pairs, electron transportability and lifetime, and the light response would be improved, thus realizing the enhanced activity, selectivity, and stability of the whole PCR systems. In addition, to further advance the photocatalytic activities of C$_3$N$_4$-based heterojunctions, the defect engineering of g-C$_3$N$_4$ would play a significant role in the pristine counterpart for artificial photosynthesis, which paves a new pathway of solar energy conversion, hence turning dreams into reality to facilitate CO$_2$-to-fuel conversion toward a breakthrough in practical applications.

Carbon-based materials such as graphene, heteroatom-doped graphene, rGO, and carbon fibers are also employed as one of the components to construct heterojunctions for the enhanced PCR performance. As a 2D nanosheet-like material, graphene could act as an electron acceptor or transporter with a large specific surface area, which efficiently separated photogenerated charge pairs in a binary system. Ali et al. prepared a nanowire-like WSe$_2$/graphene composite through an ultrasonication process, which could reduce CO$_2$ into CH$_3$OH when illuminated with UV–vis light. The proposed mechanism suggests that the charge carriers are first generated on the surface of WSe$_2$, and the photogenerated electrons transfer to the graphene nanosheets due to the high electron conductivity of the latter, thus
suppressing the recombination of the electron/hole pairs. Finally, the photoinduced electrons could reduce the adsorbed CO\textsubscript{2} into CH\textsubscript{3}OH, while the holes stored on the WSe\textsubscript{2} were responsible for H\textsubscript{2}O oxidation, respectively. When compared with 2D graphene, 3D-hierarchical nanostructured graphene with interconnected networks could provide larger surface areas and more active sites for photocatalysis. Moreover, heteroatoms (e.g., N, S) were doped into graphene, which has been regarded as a promising way to modify its electronic structure and the interactions between graphene and another semiconductor. Accordingly, Liu and co-workers fabricated a 2D/3D ZnIn\textsubscript{2}S\textsubscript{4}/N-doped graphene photocatalyst by hydrothermal synthesis,[142] which showed higher CO\textsubscript{2} photo reduction ability. The enhanced PCR performance mainly results from the broadened light absorption range from UV to near-infrared (NIR) region, rapid charge carrier separation, and selective CO\textsubscript{2} uptake capacity compared with the pristine ZnIn\textsubscript{2}S\textsubscript{4}. Importantly, the photogenerated electrons could transfer from the CB of ZnIn\textsubscript{2}S\textsubscript{4} and then accumulate onto the surface of N-doped graphene, owing to the strong electron affinity of the polar sites of N dopants, which thereby efficiently absorb CO\textsubscript{2} molecules and enable their reduction into products of CO, CH\textsubscript{4}, and CH\textsubscript{3}OH. Recently, Peng and co-workers designed a 2D/2D rGO/MOF heterojunction by cofiltering rGO nanosheets with conductive MOF nanosheets,[143] which exhibited a high CO yield rate of 3.45 \times 10^{-1} \mu\text{mol} \text{g}^{-1} \text{h}^{-1} and high selectivity of 91.74\% for CO formation after absorbing visible light. The built-in electric field at the interface of heterojunctions improves the charge harvesting and transport, as well as CO\textsubscript{2} activation (Figure 16g). The abundant charges were generated on the rGO scaffold and then transferred to the conductive and intimate interface of heterojunctions. Finally, a high density of electrons was accumulated at the Ni–N\textsubscript{4} active sites in MOF, thereby achieving highly active and selective PCR. Electrospun carbon nanofiber with 1D nanostructure shows the high specific surface area, strong conductivity, and ample reaction sites and therefore is also a promising component for a heterojunction photocatalyst. For example, Dai and co-workers reported core–shell nanostructured carbon nanofibers@TiO\textsubscript{2} nanoparticles composites,[144] which exhibited good intimate contact at the interface of hybrids, thus facilitating the charge transfer capacity and separation of the photoinduced electron/hole pairs. Moreover, the 1D morphology of the photocatalyst could provide more active sites for CO\textsubscript{2} reduction. Furthermore, the black carbon nanofibers with high conductivity could not only promote light absorption to generate heat energy for rapid diffusion of reactants and intermediates but also facilitate the separation rate of electron/hole pairs. Therefore, the system exhibited 2.3 times higher PCR activity than the pristine TiO\textsubscript{2}, which convincingly revealed the important role of carbon nanofibers.

Other metal oxides, chalcogenides, carbides, and oxysalts-based materials such as CuO/ZnO, ZnTe/ZnO, ZnS/Cds, BiFeWO\textsubscript{x}/In\textsubscript{2}S\textsubscript{3}, MoS\textsubscript{2}/BN, and Ti\textsubscript{3}C\textsubscript{2} QDs/Mexene QDs have also been designed to form heterojunctions for efficient charge separation and transportation in PCR system. For instance, CuO and ZnO nanospheres were combined to form a hierarchical p−n heterojunction via a simple hydrothermal method.[145] The as-obtained photocatalyst facilitated the separation efficiency of photoinduced electron/hole pairs and prolonged the lifetime of electrons to realize a robust CO\textsubscript{2}-to-CH\textsubscript{3}OH conversion under visible light illumination. The plausible mechanism is that CuO is activated upon visible light irradiation, and electrons and holes would generate in the CB and VB of CuO, respectively. Then, the photoexcited electrons easily transferred to the CB of ZnO, which was responsible for the reduction of carbonate species into CH\textsubscript{3}OH product. ZnTe as a typical p-type semiconductor could also connect with n-type ZnO semiconductor, forming a p−n junction due to their appropriate band structures through a facile electrochemical deposition method.[146] The resulting ZnO/ZnTe heterostructure could realize an efficient and stable CO\textsubscript{2} photoreduction, which maintained a 0.04 \mu\text{mol cm}^{-2} CH\textsubscript{4} yield during a consecutive 8 h test. The formation of Mott−Schottky junctions at the interface of ZnO/ZnTe facilitated the charge kinetics processes (generation and transferability). Metal chalcogenides have also been chosen as promising alternatives to be used in photocatalytic reactions due to their outstanding activity and low-cost properties. For instance, Wang and co-workers reported branch-like ZnS/Cds hierarchical heterostructures as highly efficient photocatalysts that could absorb visible light and provide high specific surface area,[147] abundant disclosed active sites for strong CO\textsubscript{2} absorption/capture, and accelerate the charge carrier transfer and separation ability, thus exhibiting the optimal CO formation rate of 33.3 \mu\text{mol h}^{-1}, accompanied with high durability and reusability toward the PCR reaction. In detail, CdS first absorbed the energy of visible light and generated photoexcited electrons on its CB position, and then the electrons migrated to the CB of ZnS due to their large energy difference of the CB positions between CdS and ZnS. Finally, the electrons accumulated onto the surface of ZnS and activated CO\textsubscript{2} RR. Hierarchical In\textsubscript{2}S\textsubscript{3} with a narrow bandgap of 2.0−2.3 eV and appropriate band edges has been extensively studied as an intriguing photocatalyst. In recent work, Zhong and co-workers prepared a core@shell-structured BiFeWO\textsubscript{x}@In\textsubscript{2}S\textsubscript{3} by a facile hydrothermal approach.[148] The heterojunctions enhanced CO\textsubscript{2} photoconversion to CH\textsubscript{4} and CO than that of pure BiFeWO\textsubscript{x} and In\textsubscript{2}S\textsubscript{3} under visible light illumination as the hierarchical structure improved light harvest and enriched active sites. Meanwhile, the heterojunctions could accelerate the separation efficiency and transferability of generated charge carriers. 2D nanostructural MoS\textsubscript{2} was synthesized and incorporated with h-BN nanosheets to design an h-BN-MoS\textsubscript{2} heterostructure,[149] which presented as an effective photocatalyst for CO\textsubscript{2} reduction into CH\textsubscript{3}OH under visible light irradiation. The maximum yield of CH\textsubscript{3}OH could reach up to 5994 \mu\text{mol g}^{-1} \text{h}^{-1}, which is 3.8 times higher than that of the pure MoS\textsubscript{2}. The increased PCR performance was caused by the effective separation of the photoinduced charge carriers at the interfaces between h-BN and MoS\textsubscript{2} 2D/2D heterojunctions, which not only facilitated the carrier mobility for the highly active and selective CO\textsubscript{2} photoreduction but also improved the practicability of electrons for the enhanced reduction of CO\textsubscript{2} in the whole PCR system. MXenes as a new class of 2D metal carbides, nitrides, and carbonitrides have attained increasing attention in the catalytic fields due to their optimized electronic structures, rich active sites, and good chemical stability. Accordingly, Chen and co-workers fabricated hierarchical Ti\textsubscript{3}C\textsubscript{2} QDs/Cu\textsubscript{2}O nanowire heterostructures via a progressive electrostatic method to realize a highly efficient PCR.[150] The experimental results and
theoretical calculations demonstrated that Ti$_3$C$_2$ QDs not only improved the stability of Cu$_2$O nanowires, but also enhanced the photocatalytic activity of the heterostructures by facilitating photoexcited charge transfer/separation and light absorption ability and thus showing 8.25- and 2.15-fold higher CH$_3$OH yield than that of Cu$_2$O nanowires and Ti$_3$C$_2$ nanosheets/Cu$_2$O nanowires, respectively.

### 3.2.4. Two-Step Excitation Direct Z-Scheme

Two-step excitation Z-scheme systems involve two-step excitation and charge separation processes, in which the stronger reductive electrons of one photocatalyst and the stronger oxidative holes of the other one synergistically initiate the photoredox reactions. It should be noted that the main difference between Z-scheme and type-II heterostructures is the transfer directions of the photoinduced charges of the components with different CBs and VBs (Figure 12b). The Z-scheme systems can be divided into two categories, that is, direct and indirect Z-scheme systems, and the latter employs a conductive intermediate.

In a direct Z-scheme system, the electrons generated from the CB of semiconductor I can directly combine with the holes generated from the VB of semiconductor II, and then the electrons occupied on the CB of semiconductor II with stronger reducibility can react with CO$_2$ to form carbonaceous compounds, while the holes on the VB of semiconductor I with a stronger oxidizability can promote H$_2$O/O$_2$ half reaction or sacrificial reagents. For example, α-Fe$_2$O$_3$/g-C$_3$N$_4$ hybrid acted as a hierarchical direct Z-scheme system to exhibit improved photocatalytic performance toward CO$_2$ reduction$^{131}$ which achieved a high CO production rate of 27.2 μmol g$^{-1}$ h$^{-1}$ without cocatalyst and sacrificial reagent (Figure 17a,b). The direct Z-scheme mechanism of α-Fe$_2$O$_3$/g-C$_3$N$_4$ played in PCR is shown in Figure 17c. When these two semiconductors are in direct contact, the electrons will flow from the semiconductor with a higher Fermi level to the other one through the interface until their Fermi levels are approximately similar, thus forming a built-in electric field at the interface between α-Fe$_2$O$_3$ and g-C$_3$N$_4$. The constructed electric field could cause the depletion or accumulation of free charge carriers near the semiconductor surface. Finally, the energy band edges in the semiconductor with higher Fermi levels are bent upward toward the interface, and the energy band edges in the semiconductor with lower Fermi levels are bent downward$^{152}$. Therefore the CBs and VBs of both components could be bent after an intimate contact between α-Fe$_2$O$_3$ and g-C$_3$N$_4$. The constructed internal static electric fields of α-Fe$_2$O$_3$ promoted the photoexcited electrons transferring onto the interface and combining with the holes in the VB of g-C$_3$N$_4$ and thus the reducibility of electrons in the CB of g-C$_3$N$_4$ and the oxidizability of holes in the VB of α-Fe$_2$O$_3$ increased. The electron spin resonance (EPR) was further conducted to validate the direct Z-scheme mechanism of α-Fe$_2$O$_3$/g-C$_3$N$_4$ played in PCR (Figure 17d,e). The spin reactive ·OH and ·O$_2^{-}$/C$_0$ species could absorb onto the surface of the photocatalyst and the

![Figure 17. a) TEM images of α-Fe$_2$O$_3$/g-C$_3$N$_4$ Z-scheme system. b) The CO generation rates of different photocatalysts toward PCR. c) The band energy alignment of the direct Z-scheme photocatalytic system of α-Fe$_2$O$_3$/g-C$_3$N$_4$ hybrids before and after intimate contact between the two components. DMPO spin-trapping ESR spectra tested for d) ·OH and e) ·O$_2^{-}$/C$_0$ under visible light of different photocatalysts. Reproduced with permission.$^{151}$ Copyright 2018, Wiley-VCH GmbH.](image-url)
corresponding characteristic peaks of DMPO–OH and DMPO–O₂ signals were detected. Meanwhile, the signals of the α-Fe₂O₃/g-C₃N₄ sample were much stronger than that of either α-Fe₂O₃ or g-C₃N₄. The results sufficiently demonstrated that α-Fe₂O₃/g-C₃N₄ hybrid followed the Z-scheme system rather than the conventional heterojunction type, which was demonstrated to exhibit an enhanced separation efficiency of electron–hole pairs than that of α-Fe₂O₃ or g-C₃N₄. Therefore, the hierarchical photocatalyst with Z-scheme construction broadens light absorption, improves the binding energy of CO₂ molecules, facilitates the separation of electron–hole pairs, and increases the reduction ability of photoinduced electrons, which synergistically enhance its performance toward PCR. Similarly, other photocatalysts like CsPbBr₃/[163] WO₃/[154] MoS₂/[155] Bi₂S₃/[156] SnS₂/[157] SnFeO₄/[158] NiMoO₄/[159] FeWO₄/[160] BiVO₄/[161] and Cu₃V₂O₆/[162] have also been employed to match the energy bandgap of g-C₃N₄ nanosheets, forming efficient visible light-driven Z-scheme systems for PCR. As aforementioned, g-C₃N₄-based Z-scheme photocatalysts construct a close interfacial contact between g-C₃N₄ and another semiconductor, which contributes to the improved CO₂ photoreduction into high-value-added carbonaceous compounds including CO, CH₄, CH₂OH, and HCOOH, etc. Moreover, Fei et al. provided a theoretical study for a rational-designed catalyst via element doping and Z-scheme heterojunction construction.[161] The heterojunction was composed of BiOBr and g-C₃N₄ with or without S doping, which was used for investigating the electronic effect on CO₂ reduction activity. Work function and charge density difference indicated the formation of a built-in electric field in BiOBr/g-C₃N₄ Z-scheme heterojunction, which could effectively facilitate the separation of photoinduced electron/hole pairs. Moreover, the enhanced strength of the built-in electric field was accurately analyzed by Bader charge and electric field intensity. In addition, the effect of S doping could modulate the electronic structures and thus enhance the photocatalytic performance, which was evidenced by the charge in absorption coefficient. Furthermore, analyzed by the in-depth investigation of rate-determining energy, the heterojunction with S doping preferred to generate CH₂OH than CH₄, which properly explained the selectivity of CO₂-to-fuel conversion in this system. Similar to CNs, flavin has been also regarded as a metal-free and photocative material. Savateev and co-workers reported a biomimetic core–shell structure composed of micrometer-sized flavins with potassium poly(hexamidine imide),[164] which successfully converted CO₂ molecule into CO, CH₄, MeOH, and EtOH in the water vapor atmosphere. The Z-scheme heterojunction possessed an overall wide bandgap, which significantly extended its excited states lifetimes, thus facilitating the photoredox processes and suppressing the interface charge recombination.

In addition, other direct Z-scheme systems such as ZnIn₂S₄/TiO₂,[156,157] BiOBr/NiO,[167] Cu₃O/TiO₂,[168] rGO/TiO₂,[169] NiFe LDH/CuO,[170] BiVO₄/CuO,[171] WO₃/CuO,[172] and Cu₃ZnSnS₂/ZnO[173] have been proposed to realize the enhanced activity for PCR. For example, Yu’s group reported a step-scheme core–shell TiO₂@ZnIn₂S₄ heterojunction,[166] which exhibited much higher catalytic performance than that of pure TiO₂ or ZnIn₂S₄ in CO₂ photoreduction. Due to the large specific surface areas, abundant active sites, and Z-scheme structure, the catalyst showed highly efficient conversion of solar fuels due to the improved separation of photogenerated charge carriers, which was evidenced by in situ XPS, work function calculation, and EPR measurements. The group also reported a novel Z-scheme BiOBr/NiO catalyst composed of two kinds of p-type semiconductors,[167] which could achieve enhanced CO₂ photoreduction activity than that of BiOBr or NiO. Analyzed by the in situ XPS and work function calculation, the photoinduced electrons transferred from BiOBr to NiO via a Z-scheme mechanism, which contributed to a strong redox ability and enhanced change separation. Meanwhile, in situ DRIFT spectra revealed the formation of complex intermediates during the CO₂ photoreduction process. These results provided a new insight for the CO₂ photoreduction mechanism in Z-scheme heterojunctions constructed by p-type semiconductors. These newly developed Z-scheme photocatalytic systems realize efficient and stable CO₂ conversion into CH₄ or CO with a high yield and formation rate.

3.2.5. Two-Step Excitation Indirect Z-Scheme

Different from the direct Z-scheme system, a third component such as noble metal or graphene oxide has been incorporated as an indispensable conductive intermediate to facilitate the charge transfer and separation of electron/hole pairs in indirect Z-scheme system. To this end, systems such as ZnO/Au/g-C₃N₄,[174] ZnCdS/Au/g-C₃N₄,[175] SnS₂/Au/g-C₃N₄,[176] ZnFeO₄/Ag/TiO₂,[177] Cu₂O/Ag/ZnO,[178] AgPO₄/Ag/CeO₂,[179] α-Fe₂O₃/amine–rGO/CsPbBr₃,[180] ZnFeO₄/rGO/In₂O₃,[181] Bi₂WO₆/rGO/g-C₃N₄,[182] have been constructed and investigated in PCR, where photoexcited electrons transfer from semiconductor I to conductive intermediate and then to semiconductor II, resulting in enhanced charge separation and improved redox reactions. Recently, Li et al. reported a Z-scheme ZnO/Au/g-C₃N₄ film photocatalyst with an LSPR effect for CO₂-to-CH₄ conversion under UV–vis light illumination.[174] Verifier by DFT calculations and finite-difference time domain (FDTD) method, it can be concluded that the g-C₃N₄/N₂ O interface builds the electric field to facilitate carrier mobility. Meanwhile, the Au nanoparticles not only acted as a conductive active intermediate for the vectorial electron transfer but also as the LSPR source to promote the separation efficiency of electron–hole pairs and optical response range. Accordingly, the ZnO/Au/g-C₃N₄ photocatalyst maintained a high CO formation rate of 689.7 μmol m⁻² during a consecutive 8 h reaction time, which was significantly higher than that of pure ZnO film (155.5 μmol m⁻²). Kuang’s group designed an all-solid-state Z-scheme α-Fe₂O₃/amine–rGO/CsPbBr₃ hybrid for highly efficient PCR (Figure 18a,b).[180] The photocatalyst showed a stable product (CH₄ + CO) yield of 469.16 μmol g⁻¹, which was 8.3 times higher than that of pristine CsPbBr₃ (Figure 18c). The amine–rGO could effectively regulate the interfacial interaction between CsPbBr₃ and α-Fe₂O₃ and then facilitate the transfer of photogenerated carriers from α-Fe₂O₃ to CsPbBr₃ through amine–rGO, therefore contributing to the enhanced separation of electron–hole pairs. Moreover, CsPbBr₃ and α-Fe₂O₃ played the roles of photocatalyst I and photocatalyst II, respectively, which showed a wide light-absorption capability and suitable reduction and oxidation potential, leading
to an improved catalytic activity toward CO2-to-CH4/CO conversion with an approximately stoichiometric amount of O2 formation. The above research work demonstrated that the indirect Z-scheme composed of ternary materials could not only facilitate the transferability of charge carriers but also widen the light response and therefore promote the development of efficient PCR into high added-value carbonaceous chemicals and fuels.

4. Photothermocatalysis

4.1. Motivation and Principles

The conventional thermocatalytic CO2 hydrogenations require high energy consumption and system pressure, while the PCR rarely provides high-energy photons to sufficiently activate CO2 conversion toward multicarbon chemicals and fuels production. Accordingly, the integration of these two techniques in a hybrid system is regarded as a promising route for highly efficient CO2 reduction, which simultaneously utilizes solar energy and heat energy to initiate the reaction. When an effective catalyst (especially the sample with black color) is irradiated upon light illumination, the light energy (e.g., visible and near-infrared light) can dissipate into heat energy, which can operate the conventional thermocatalytic reactions under mild conditions. Note that the surface temperature of the catalyst can reach up to 500 °C or even higher, which offers efficient energy to conduct the thermodynamically unfavorable CO2 reduction. The catalysts used in photothermocatalysis have been generally classified into two categories: plasmonic metals and other systems. The plasmonic metal system plays the LSPR effect, which contributes to elevated electric fields on the catalyst surface, and thereby resulted in a high density of energetic charge carriers, mainly hot electrons and holes after nonradiative decay through intraband or intraband excitations (Figure 19a). The photoexcited hot electrons could promote bond activation and intermediate conversion in CO2 reduction. In detail, the hot electrons transform the reactant molecules along an exciting potential energy surface, which contributes to extra vibration energy to the reactant, thereby activating the molecular bonds (Figure 19b). When referred to the intermediate evolution, both direct and indirect routes play critical roles in optimizing the reaction selectivity and activity (Figure 19c,d).[9] Other systems without LSPR effects could also perform efficient activities in photothermocatalysis, mainly depending on the structural optimization of the catalysts. However, the mechanism of photothermocatalysis is complex due to unknown thermodynamics and kinetics, and the synergy between the photocatalytic and thermal effects remains unexplored. In general, the newly developed photothermocatalysis could overcome the difficulties of inferior activity in photocatalysis and excess reaction barriers in thermocatalysis, with abundant solar energy under lower temperatures and pressures.

4.2. Plausible Routes for CO2 Hydrogenation

The primary reactions evolved in photothermocatalysis can be broadly classified into five groups: 1) RWGS reaction, 2) methanol and ethanol synthesis, 3) methanation reaction, and 4) CO2 hydrogenation. Some aspects are similar to thermocatalysis, which have been reviewed in Section 2.1.

4.2.1. CO2 to CO

1. In the thermocatalytic RWGS reaction, some transition metals and metal oxides have been studied to produce CO via CO2 hydrogenation under certain temperatures and pressures. It should be noted that the photothermocatalytic RWGS reaction concentrates on nanostructured materials, which exhibited distinguished catalytic performance. For example, Ozin and co-workers designed a black indium oxide catalyst via hydrogenating In2O3 NC,[183] thus forming amorphous domains of In2O3+...x on...
Figure 19. a) The illustration of hot carriers generated through nonradiative decay that resulted from the LSPR effects. b) Bond activation over plasmonic metals. Immediate conversion after absorbing the plasmon energy from the metal in an c) indirect and d) direct route, respectively. Reproduced with permission.[9] Copyright 2019, Wiley-VCH GmbH.

Figure 20. a) HRTEM image of the nonstoichiometric In$_{2}$O$_{3-x}$ after annealing stoichiometric In$_{2}$O$_{3}$ NC at 400 °C under N$_{2}$ and H$_{2}$ atmosphere for 20 min. b) Illustration of the treated In$_{2}$O$_{3}$. Pink dots, yellow dots, yellow circles, and blue regions represent In atoms, O atoms, oxygen vacancies, and amorphous phase, respectively. c) The performance of In$_{2}$O$_{3-x}$/In$_{2}$O$_{3}$ prepared by different treated times in photothermocatalytic CO$_{2}$ hydrogenation in a batch reactor. S1 indicates the as-prepared In$_{2}$O$_{3}$ NC. S2, S3, and S4 are obtained by annealing pristine S1 under H$_{2}$ atmosphere at different temperatures (i.e., 200, 300, and 400 °C) for 1 h to form In$_{2}$O$_{3-x}$/In$_{2}$O$_{3}$ with different x values. d) Schematic illustration of the electronic band structure of In$_{2}$O$_{3-x}$/In$_{2}$O$_{3}$ heterojunction under light illumination. Reproduced with permission.[183] Copyright 2020, Springer Nature. e) HRTEM image of Al/Al$_{2}$O$_{3}$/Cu$_{2}$O heterostructure. f) The CO production rates of Al/Al$_{2}$O$_{3}$/Cu$_{2}$O versus visible light intensity in photothermocatalytic RWGS reaction. g) Schematic mechanism of plasmon-driven RWGS reaction using Al/Al$_{2}$O$_{3}$/Cu$_{2}$O heterostructures. Reproduced with permission.[185] Copyright 2017, Springer Nature.
crystalline In2O3 (Figure 20a,b). The constructed nonstoichiometric/stoichiometric In2O3-x/In2O3 heterojunction enabled high activity for RWGS reaction with 100% selectivity toward CO formation, which achieved an extremely high CO production rate of 1874.62 μmol h⁻¹ m⁻² (23882.75 μmol g⁻¹ h⁻¹) (Figure 20c), three orders of magnitude higher than pale yellow In2O3 (19.64 μmol g⁻¹ h⁻¹) under 100 W LED white lamp. The significantly enhanced performance could be ascribed to the synergistic roles of stronger sunlight absorption ability and photo-thermal effects. The oxygen vacancies in In2O3-x promoted the insertion of protons to weaken the C−O bonds of the CO2 reactant, which facilitated the CO formation (Figure 20d). Meanwhile, the In2O3-x/In2O3 heterostructure enhanced the light absorption across the solar spectrum, which gave rise to local heating on the surface of the catalyst and then contributed to the thermocatalytic conversion of the RWGS reaction. Moreover, the heterostructure could effectively separate photoinduced electron–hole pairs, which also contributed to the enhanced PCR performance. Therefore, the surface black In2O3-x layer acted as promising material to perform an improved activity in photothermal RWGS reactions. Recently, Ozin and Zhang and co-workers reported a supraphotothermal Ni@p-SiO2 catalyst, which exhibited a satisfying catalytic activity and stability toward RWGS and methanation reactions due to the spatial confinement effects, heat insulation, and infrared shielding effects of catalysts. Halas and co-workers reported the synthesis of Al/Al2O3/Cu2O heterostructures (Figure 20e), which exhibited highly efficient and selective RWGS activity under light irradiation at room temperature than that in thermal conditions (Figure 20f). To investigate the spatial temperature, light absorption ability, and integrated electric field of the heterostructural catalyst, the work demonstrated that the LSPR effect of Al@Cu2O antenna reactors could provide abundant hot carriers and broaden the light absorption range of Cu2O under visible light illumination, thereby achieving highly selective CO production in CO2 conversion. Al@Cu2O acted as the active component exhibiting plasmon-enhanced CO2 conversion, which was accompanied by heat generation from the thermalization of the hot carriers, thus resulting in an enhanced photo-thermocatalytic process (Figure 20g). The local temperature of Al/Al2O3/Cu2O surface could reach up to 175 °C under visible light irradiation due to the photothermal heating from electron–electron scattering during the hot-carrier decay. The photoinduced hot carriers flowed from Al core to Cu2O shell, which played the main role in C−O bond dissociation and prolonged the lifetime of excited states. Accordingly, the Al@Cu2O antenna receptor mechanism was proposed, which achieved higher activity and selectivity in the RWGS reaction than the traditional thermocatalysis, and thus showed an optimal CO formation rate of 360 μmol C O cm⁻² s⁻¹ during the light-excited process (10 W cm⁻²).

Other catalysts have also been reported for efficient CO2 photothermolysis, such as TiO2@In2O3-x(OH)y, Cu hydroxypatite, W-doped TiO2, Pd/TiO2, FeO–CeO2, MoO3-x, Bi2TaO6Cl/W19O64, Bi2S3/Uio-66, Co@CoNiC, Ni12P5, and Pd nanoparticle (NPs)/barium titanate, which reached satisfying CO formation rates upon solar light illumination.

4.2.2. CO2 to Alcohols

In comparison with photothermocatalytic RWGS reaction, studies on methanol and ethanol synthesis are quite limited. Hong and co-workers designed a Pd/ZnO catalyst through a facial impregnation approach to realize industrial MeOH formation at relatively low pressure (12 bar) under light irradiation. The enhanced MeOH yield was due to the synergy effect between photocatalysis and thermocatalysis, as well as a wide visible light absorption range induced by the LSPR effect of Pd nanoparticles (Figure 21a–c). The latter was confirmed to be the main contributor (>90%) to the enhanced photothermocatalytic MeOH formation. The interface of Pd–ZnO would accept the abundant hot electrons and acted as the active site to promote CO2 absorption and activation via electron injection to the antibonding orbital of CO2 molecules, thus resulting in MeOH synthesis in a similar way to thermocatalytic CO2 hydrogenation. Therefore, Pd/ZnO achieved a promotion of CO2 conversion efficiency more than two times and enhanced yield of MeOH (1.5–3.0 times) under light irradiation in a flow fixed-bed plasmon-assisted photothermal reactor under relatively lower pressure. Some other catalysts including Cu7Cu2O, CoO/Co/TiO2, and LaCo2Fe13–xOy have been reported to achieve efficient MeOH synthesis through plasmon-assisted photothermocatalysis or photo–thermo coupling conditions (Table 1). For example, Cui’s group fabricated a complex composed of Au/Cu alloy nanoparticles and ultrathin porous g-C3N4 nanosheets (Figure 21d) and the integrated photocatalysis and thermocatalysis synergistically realized an enhanced yield (0.89 mmol g⁻¹ h⁻¹) and selectivity (93.1%) of ethanol formation at 120 °C under visible light irradiation using 1.0 wt% Au/Cu/g-C3N4 composites (Figure 21e). The positive charges on Au surface facilitated CO2 adsorption, while Cu with enriched negative charges improved the *CO and *CO2 intermediate generation. Meanwhile, the strong interaction between Au/Cu alloy and g-C3N4 promoted photoinduced carrier transportation. Moreover, the increased temperature on the surface of the catalyst accelerated the dynamics and thermodynamics of reactant molecules, which resulted in the enhanced *CO and *CO2 dimeterization and C–C coupling reactions (Figure 21f). Accordingly, the Au/Cu/g-C3N4 catalyst exhibited 4.2- and 7.6-fold higher yield toward photothermocatalytic ethanol synthesis than that in photocatalytic and thermocatalytic processes, respectively.

4.2.3. CO2 to CH4

Methanation reaction is known as the Sabatier reaction, which can produce CH4 via CO2 hydrogenation. Ru- and Ni-based materials have been the most frequently used catalysts for CO2 methanation to realize the satisfying CH4 yield and selectivity. Ye’s group constructed a hybrid catalyst with small Ru nanoparticles supported on ultrathin Mg–Al few-layer LDHs (Mg–Al FL-LDH) supports (Figure 22a,b) which could reach a peak rate of CH4 formation (277 mmol g⁻¹ h⁻¹) in a flow-type reactor (Figure 22c, d). The Ru nanoparticles played vital roles in H2 activation and the subsequent CO2 hydrogenation as metallic Ru could enhance the local temperature of the Ru@FL-LDHs surface after absorbing solar light. Meanwhile, ultrathin Mg–Al LDH possessed
abundant active sites, which benefited the CO2 activation and reactant absorption. A series of control experiments had been conducted to reveal the mechanism of photothermocatalytic processes in this work. Light illumination is regarded as a driving force to initiate the photo-to-thermal conversion, while photocalysis played a negligible role in CH4 production. In other words, the photothermal reaction is quite similar to that in the traditional thermocatalysis, where Ru@FL-LDHs reached a high reaction temperature of $\approx 350^\circ C$ under continuous irradiation to activate H2 molecules. Moreover, the close intact nature between Ru nanoparticles and FL-LDHs certainly contributed to the highly efficient CO2 hydrogenation process. Therefore, Ru@FL-LDHs performed an efficient and stable methanation reaction toward CO2 photothermolysis under mild reaction conditions. In addition to Ru, Ni as an abundant and low-cost material has been employed as an active catalyst for photothermocatalytic CO2 methanation. Accordingly, Li et al. realized satisfying CO2 methanation performance by developing a new photothermal reactor with the presence of a layer of absorber (Figure 22e). Under solar light illumination (from 0.52 to 0.7 kW m$^{-2}$), the catalyst that was composed of single Ni atoms, and ultrathin amorphous Y2O3 nanosheets (the SA Ni/Y2O3 nanosheets) (Figure 22f) showed an optimal CH4 formation yield up to 7.5 L m$^{-2}$h$^{-1}$ with a high CO2 conversion efficiency of 80% under elevated temperature (Figure 22g,h). The rational design of single-atom Ni coupled with the selective light absorber (here ultrathin amorphous Y2O3 nanosheets) could realize a high and stable photothermocatalytic methanation reaction under solar light irradiation at a relatively lower initial reaction temperature using SA Ni/Y2O3 composites. The Co species also exhibits a high photothermo effect in CO2 methanation as it can absorb the solar light and then convert it to thermal energy via the intra- and interband electron transition. It means that photoexcited electrons could recombine with the holes to generate phonons rather than photons, which increases the local temperature on the surface of Co-based catalysts and thereby performs good activity in photothermocatalytic CO2 methanation under solar light irradiation. Herein, Jia’s group fabricated highly dispersed Co nanoparticles on Al2O3 support (Figure 23a), which achieved an extraordinary CH4 formation rate of $6036 \mu$mol g$^{-1}$ h$^{-1}$ with high CH4 selectivity of 97.7% during continuously catalytic testing (Figure 23b,c). The broad optical response range, the strong adsorption ability toward reactant molecules, and the large density of active sites synergistically contributed to the enhanced photothermocatalytic performance of Co/Al2O3. Moreover, the UV–vis light irradiation promoted the formation of oxygen vacancies on the surface of Co/Al2O3, which improved the adsorption ability of CO2 molecules.
### Table 1. Performance comparisons of the representative catalysts used in photothermocatalytic CO₂ hydrogenation under light irradiation.[183,185–197,199–218]

| Catalyst | Light source | Temperature[^a] | Production rate | Ref. |
|----------|--------------|-----------------|-----------------|------|
| RWGS reaction (product: CO) | | | | |
| Ir₂O₃–/IrO₂ | 100 W LED white lamp | 300 °C | 1874.62 μmol h⁻¹ m⁻² | [183] |
| Al(Al₂O₃)/Cu₂O | White light, 10 W cm⁻² | 175 °C | 360 μmolCO cm⁻² s⁻¹ | [185] |
| TiN@CoO/TiO₂ | Xe lamp | 150 °C | 5.35 μmol cm⁻² h⁻¹ | [186] |
| TiN@TiO₂@In₂O₃/OH | Xe lamp, 1.6 W cm⁻² | 225 °C | 3439.9 μmol g⁻¹ h⁻¹ | [187] |
| 2D Ir₃O₁₋ₓ | 300 W Xe lamp | 370 °C | 103.2 mmol g⁻¹ h⁻¹ | [188] |
| Cu hydroxypatite | 40 sun | | | [189] |
| 4%W-doped TiO₂ | UV light | 120 °C | 0.056 μmol g⁻¹ h⁻¹ | [190] |
| 1.0 wt% Pd/TiO₂ | 500 W Mercury light, >254 nm | 500 °C | 11.05 μmol g⁻¹ h⁻¹ | [191] |
| FeO–CeO₂ | Xe lamp, 2.2 W cm⁻² | | 19.61 mmol g⁻¹ h⁻¹ | [192] |
| MoO₃ | UV–vis–IR light | 160 °C | 10.3 μmol g⁻¹ h⁻¹ | [193] |
| Bi₂TaO₅Cl/W₁₈O₄₉ | Solar light, 180 mW cm⁻² | 120 °C | 23.42 μmol g⁻¹ h⁻¹ | [194] |
| 1.9%Bi₂S₃/UO-66 | Solar light 650 mW cm⁻² | 150 °C | 25.60 μmol g⁻¹ h⁻¹ | [195] |
| Co@CoN/C | 300 W Xe lamp | 518 °C | 132 mmol g⁻¹ h⁻¹ | [196] |
| Ni₃P₅ | Xe lamp 2.3 W cm⁻² | | ≈960 mmol g⁻¹ h⁻¹ | [197] |
| Alcohol synthesis (products: MeOH and EtOH) | | | | |
| Pd/ZnO | 500 W Mercury light | 270 °C | MeOH: ≈4.5 mmol g⁻¹ h⁻¹ | [199] |
| Cu⁺/Cu⁺ | 300 W Xe lamp, λ > 400 nm | 110 °C | MeOH: 2.6 μmol g⁻¹ h⁻¹ | [200] |
| CoO/Co/TiO₂ | 300 W Xe lamp | 120 °C | MeOH: 39.6 μmol g⁻¹ h⁻¹ | [201] |
| LaCo₂Fe₉O₄ | 300 W Xe lamp, λ > 420 nm | 350 °C | MeOH: 2.3 μmol g⁻¹ h⁻¹ | [202] |
| AuCu₆/C₆N₄ | 300 W Xe lamp, λ > 420 nm | 120 °C | EtOH: 895 μmol g⁻¹ h⁻¹ | [203] |
| Methanation reaction (product: CH₄) | | | | |
| Ru@FL-LDHs | 300 W Xe lamp, 10 Suns | 350 °C | 277 mmol g⁻¹ h⁻¹ | [204] |
| Single Ni atom/Y₂O₃ | Solar irradiation, 1 kW m⁻² | 288 °C | 7.5 L m⁻² h⁻¹ | [205] |
| 21%Co/Al₂O₃ | UV–vis–IR light, 1300 mW cm⁻² | 292 °C | 6036 μmol g⁻¹ h⁻¹ | [206] |
| Amorphous boron | 300 W Xe lamp | 378 °C | 2.5 μmol h⁻¹ | [207] |
| TiO₂ Pcs | 300 W Xe lamp | 2 °C | 35.0 μmol g⁻¹ h⁻¹ | [208] |
| Ru₃–Si–o | 300 W Xe lamp, 2470 mW cm⁻² | 150 °C | 2.8 mmol g⁻¹ h⁻¹ | [209] |
| Ni NPs/BaTiO₃ | 300 W Xe lamp, 293 mW cm⁻² | ≈335 °C | 103.7 mmol g⁻¹ h⁻¹ | [210] |
| Ni/BOC-20Tl-5G | 300 W Xe lamp | >200 °C | 17.0 mmol g⁻¹ h⁻¹ | [211] |
| TiO₂ NPs/Graphene | 300 W Xe lamp, 4.38 kW m⁻² | 116.4 °C | 26.7 μmol g⁻¹ h⁻¹ | [212] |
| TiO₂@P/C | 150 W UV lamp | 120 °C | ≈10 μmol g⁻¹ h⁻¹ | [213] |
| C₂ + hydrocarbons synthesis | | | | |
| Fe-500 | 300 W Xe lamp, 1.88 W cm⁻² | 252–312 °C | CH₄: 47.1% | [214] |
| C₂: 46.6% | | | | |
| α-Fe₃C | 300 W Xe lamp, 2.05 W cm⁻² | 310 °C | CH₄: 10.9 mmol g⁻¹ h⁻¹ | [215] |
| Fe₂O₃/Fe₇O₄ | Highly concentrated sunlight (concentrating ratio: 600) | 500 °C | CH₄: 1470.7 μmol g⁻¹ h⁻¹ | [216] |
| C₂H₄: 736.2 μmol g⁻¹ h⁻¹ | | | | |
| C₂H₆: 277.2 μmol g⁻¹ h⁻¹ | | | | |
| Na/Co@C | 1000 W Xe lamp, AM 1.5 filter | 235 °C | CH₄: 50.2% | [217] |
| C₂: 13.0% | | | | |
| C₂: 12.7% | | | | |
| C₂: 5.2% | | | | |
| C₂: 3.3% | | | | |
| C₂: 2.0% | | | | |
Table 1. Continued.

| Catalyst                  | Light source | Temperature | Production rate | Ref.          |
|---------------------------|--------------|-------------|-----------------|---------------|
| Ni-doped BaZr0.5Ce0.3Y0.2O3–δ | UV light     | 350 °C      | CH4: 219.9 μmol g⁻¹ | [218]         |
|                           |              |             | C2H6: 83.24 μmol g⁻¹ |               |
|                           |              |             | C3H8: 12.7 μmol g⁻¹ |               |
| Co-doped BaZr0.5Ce0.3Y0.2O3–δ | UV light     | 350 °C      | CH4: 266.8 μmol g⁻¹ |               |
|                           |              |             | C2H6: 123.2 μmol g⁻¹ |               |
|                           |              |             | C3H8: 21.27 μmol g⁻¹ |               |

The equilibrium temperature values of the samples under focused light irradiation; “…” indicates not noted.

Figure 22. a, b) TEM and HRTEM images of Ru@FL-LDHs catalyst. c) The CH4 yield over Ru@FL-LDHs catalyst under 300 W Xenon lamp irradiation (light intensity, 10 Suns) at H2/CO2 flow rates of 25.0 and 5.0 mL min⁻¹, respectively. d) Schematic illustration of photothermocatalytic CO2 hydrogenation processes over Ru@FL-LDHs catalyst in a flow reactor. Reproduced with permission.[204] Copyright 2017, Wiley-VCH GmbH. e) Schematic illustration of the newly developed photothermocatalytic reactor system for CO2 methanation with the selective absorber and the SA Ni/Y2O3 nanosheets. f) STEM image and the corresponding EDS mapping images of Ni, Y, and O of the SA Ni/Y2O3 nanosheets. g) The spatial temperature mapping of the newly developed photothermocatalytic system under simulated solar light illumination using an infrared camera (intensity: 1.0 kW m⁻²). h) The performance of the SA Ni/Y2O3 nanosheets catalyzed in photothermocatalytic CO2 hydrogenation. Reproduced with permission.[205] Copyright 2019, Springer Nature.
thus facilitating the CO₂ conversion into CH₄ product. Furthermore, the Al₂O₃ support with high surface area and porosity also played an essential role in improving the CH₄ production yield, selectivity, and stability. Except for metallic catalysts, other materials like boron, TiO₂, and their heterojunctions have also been investigated in photothermocatalytic process. For example, Ye’s group reported a fascinating approach to design the elemental B particles for the first time (Figure 23d), which showed high light-response ability and efficient photo-thermal conversion. The photothermal effect of B particles could elevate the local temperature of the catalysts to activate CO₂ molecules. Meanwhile, the self-healing ability of the B element under light irradiation could decompose H₂ molecules and provide an active proton source as well as electrons for CO₂ reduction. In conclusion, elemental B catalyst exhibited a CH₄ production rate of 2.5 μmol h⁻¹ in the presence of water without any sacrificial agents or cocatalyst under UV–vis–IR light illumination (Figure 23e,f), which opened up a new era toward highly efficient CO₂ conversion and solar light utilization. Yu’s group employed a facile strategy to design TiO₂ photonic crystals (TiO₂ PCs) through an anodization–calcination process (Figure 23g,h), which possessed the satisfying heat radiation capture ability. With the specific PC morphology, the TiO₂ PC catalyst showed localized surface photothermo effect (Figure 23i), which not only improved light absorption but also increased the surface temperature to accelerate reaction kinetics and product yield rates, finally contributing to a high CO₂ methanation rate of 35.0 μmol g⁻¹ h⁻¹, superior to that of commercial TiO₂ or TiO₂ nanotube arrays. Except for the aforementioned catalyst, some other materials such as Ru/i–Si–o[209] Ni NPs/BaTiO₃[210] Ni/Fe–Ti,[211] TiO₂ NPs/graphene[212] and
TiO$_2$–x/CoO$_x$\textsuperscript{[213]} have been recently reported for enhanced activity and selectivity for photothermocatalytic CO$_2$ methanation.

4.2.4. CO$_2$ to C$_2$+ Hydrocarbons

The direct hydrogenation of CO$_2$ into hydrocarbons is a promising route to produce valuable CH$_x$ chemicals. Fe-based catalysts have been regarded as ideal alternatives used in photothermocatalytic CO$_2$ hydrogenation to produce multicarbon hydrocarbons under solar light illumination at atmospheric conditions. Zhang’s group proposed a Fe-500 catalyst composed of Fe and FeO$_x$ nanoparticles on a MgO–Al$_2$O$_3$ support (Figure 24a–c),\textsuperscript{[214]} which showed satisfying performance toward CO$_2$-to-C$_2$+ hydrocarbon conversion with high CO$_2$ conversion (50.1%) and C$_2$+ selectivity (52.9%) when irradiated by UV–vis light (Figure 24d). Evidenced by the experimental results and DFT calculations, the construction of Fe/FeO$_x$ heterojunctions suppressed the –CH$_2$ and –CH$_3$ hydrogenation to CH$_4$ on the active Fe$^0$ species. On the contrary, it facilitated the CO$_2$ hydrogenation into CO and the subsequent C–C coupling (Figure 24e), thereby improving the selectivity of C$_2$+ hydrocarbons production. Meanwhile, the local surface temperature of Fe-500 could rapidly increase up to 252°C under Xe lamp irradiation, which achieved almost the same activity as that in the thermocatalytic CO$_2$ conversion. Moreover, the light density is demonstrated to show negligible impact on CO$_2$ conversion or

Figure 24. a) TEM image, b) the corresponding EDS elemental mapping of Fe, Mg, Al, and O, and c) HRTEM image of Fe-500 catalyst. d) Product selectivities (i.e., CH$_4$, C$_2$–4, and C$_5$+) and CO$_2$ conversion over Fe-500 catalyst under UV–vis illumination under a flow test. e) The energy profiles of the C–C coupling pathways on 3O/Fe(110) and Fe(110). The blue, black, red, and white spheres represent Fe, C, O, and H atoms, respectively. Reproduced with permission.\textsuperscript{[214]} Copyright 2021, Wiley-VCH GmbH. f) Schematic illustration of the photothermocatalytic CO$_2$ hydrogenation to CH$_4$, C$_2$+ hydrocarbons, and ethanol using Na-Co@C catalyst. Reproduced with permission.\textsuperscript{[217]} Copyright 2018, Elsevier B.V.
C₂⁺ selectivity, which indicated that the CO₂-to-C₂⁺ conversion on Fe–500 catalyst followed a photothermocatalytic mechanism instead of photocatalysis. Other Fe-based catalysts (e.g., θ-Fe₃C[215] and Fe₂O₃/Fe₃O₄[216]) have also been investigated in photothermocatalytic CO₂ hydrogenation, which reached extraordinary selectivity for C₂⁺ hydrocarbons formation. Furthermore, metallic Co, and Ni have also been employed in the CO₂ hydrogenation to generate C₂⁺ hydrocarbons through the photothermocatalytic processes. For example, Na–Co@C[217] (Figure 24f) and Ni- or Co-doped BaZr₀.₅Ce₀.₃Y₀.₂O₃[218] have been employed as efficient materials to enhance the surface temperature, photoexcited electron mobility, CO₂ dissociation, absorption ability of CO, C–C coupling, and the rapid desorption of reaction products onto the surface of catalysts, which synergistically contributed to the highly efficient photothermocatalytic CO₂ hydrogenation to C₂⁺ hydrocarbons. These studies could guide the design of efficient catalysts for artificial photosynthesis via photothermocatalytic CO₂ hydrogenation, which can finally produce high-value-added multicarbon chemicals and fuels from CO₂.

5. Conclusion and Perspectives

The efficient utilization and chemical transformation of CO₂ into value-added chemicals and fuels have received increasing attention and been regarded as a promising approach to alleviate global warming, energy, and environmental crises. Notably, solar-driven photocatalysis has presented significantly enhanced activities and selectivities, which cater to the scientific and industrial communities and can be comparable with traditional thermocatalysis. This review primarily outlines the state of the art of the technologies toward thermocatalytic, photocatalytic, and integrated photothermocatalytic CO₂ conversion into products of CO, CH₄, formate, methanol, ethanol, and C₂⁺ hydrocarbons/oxygenates in the past 5 years (Figure 25). Special focuses have been paid to the designing strategies for effective heterogeneous catalysts for selective CO₂ conversion. Although the processes of thermocatalytic CO₂ hydrogenation into C₁ chemicals (e.g., MeOH, CH₄) have been commercialized, the achievements in CO₂ chemical transformations are still not satisfactory concerning the technical and economic viability and energy efficiency for large-scale employment. Accordingly, extensive investigations have been conducted to develop UV and/or visible light-sensitive semiconductors for photocatalytic and photothermocatalytic CO₂ conversion. Particularly, plasmonic photocatalysis and plasmonic photothermocatalysis not only occupy an important position in practical CO₂-to-fuels conversion with a high utilization efficiency of solar energy but can also reference the selection of catalysts and reaction conditions from the conventional thermocatalysis, which builds a strong bridge between photocatalysis and conventional thermocatalysis. Moreover, the distinct pathways toward different products of these techniques have been comprehensively summarized to reveal the reaction mechanisms and key steps that determine the formation of the intermediates and final products, which can further serve as the guidance for the rational design of catalytic systems. Regardless of the aforementioned achievements, there is still plenty of room to improve the catalytic performance in the community of thermocatalysis and photo(thermo)catalysis.

More challenges should be overcome toward the following aspects. 1) It is highly demanded to develop highly active and cost-effective catalysts for large-scale synthesis, such as layer double hydroxides with tunable band structure and oxides/nitrides.
with optimized geometric effect. 2) The yields and selectivities of C₂ hydrocarbons and oxygenates are more desired, although most of the existing catalytic systems produce C₁ chemicals (e.g., CO, formate, CH₄). The synthesis of C₂ hydrocarbons and oxygenates needs to overcome the thermodynamic limits and kinetic barriers during the multielectron transfer processes in CO₂RR, which will relieve excessive energy consumption and improve the energy conversion efficiency of the current CO₂ conversion techniques. Importantly, CO₂ adsorption, activation, and *CO intermediate formation significantly determine the yield of C₂ products. For example, the *CO dimerization affects the production rates of C₂H₄, ethanol, and n-C₃H₇OH. The *CH₃CHO intermediate generated from the *CO–CO dimerization is the rate-determining step for C₂H₄ and C₂H₅OH formation. Furthermore, n-C₃H₇OH can be produced by inserting CO into the stabilized *CH₃CHO intermediate. Therefore, the selectivities of targeted C₂ products have to be well controlled by the rational design of nanostructured catalysts. Intelligent strategies can be employed, such as morphology and structure optimization, alloying/dealloying, surface modification, and support introduction. Meanwhile, the structural integrity of catalysts and long-term durability of the overall catalytic systems still require to be improved for practical application as most durability tests have been conducted for a few hours and deactivation analyses are quite scarce. For example, thermal stability and recyclability of thermocatalysts have been tough problems to be resolved. Meanwhile, to suppress the photocorrosion and enhance the durability of (photo)thermocatalysts in the aqueous solution, coating the surface of the catalysts with protective layers through atomic layer deposition or electron beam evaporation methods may substantially improve the system stability for large-scale application. Accordingly, the structure of the catalysts, reaction conditions, and reactor configurations are required to be carefully designed for the improvement of the long-term catalytic system. 3) In terms of solar-driven photocatalysis, the intensity of the light source used in the lab (e.g., Xe lamp, Hg lamp) is much greater than sunlight. Moreover, the natural day/night cycle and narrow light absorption ability of most photo(thermo)catalysts not only bring challenges for industrial application but also reduce the utilization of solar energy. Accordingly, some ideal catalysts, such as rare-earth upconversion luminescent materials, photothermal semiconductors with a black color, or high density of defects/vacancies, can be designed to directly convert solar light to heat energy and applied in CO₂ hydrogenation, which not only elevates the photochemical contribution but also enhances the charge transfer efficiency and photoinduced carrier lifetimes, thus improving the catalytic activity. 4) Adequate photoreactors are required to effectively absorb and utilize sunlight for photo(thermo)catalysis, and therefore the continuous flow systems can be rationally designed to meet the requirements of industrial applications. 5) A standardized metrology method requires to be created to evaluate the solar-to-chemical conversion efficiency in photocatalytic and photothermocatalytic CO₂ reduction so that the comparison of the results from different research groups is convincing and fairly. Meanwhile, the intrinsic photocatalytic effect and photothermal effect should be identified. The key is to distinguish the thermal and nontermal effects in photothermocatalysis, which can be measured by a precise instrument like nanoscale thermometers. 6) Computational analysis through DFT is of great significance to complement the experimental characterizations, which contributes to revealing the structure—activity relationship of the system and identifying the active sites, intermediate species, reaction pathways, and the roles of additives and water for CO₂RR.

Generally, as catalysts stand at the center to realize improved activity, selectivity, structure stability, and long-term durability, significant advances in designing effective heterogeneous catalysts are required for practical applications. The demonstrated strategies include structure optimization, crystal facets regulation, and defect engineering, thereby exposing increased density of active sites, high specific surface area, and closely conjoint interfaces to facilitate CO₂ adsorption and the subsequent transformations. Moreover, the reaction conditions and reactor design are always ignored, which need to be optimized to satisfy energy transfer (e.g., heat, light) and simplify equipment demand, aiming at constructing a well-established system for the enhancement of overall CO₂RR performance. Furthermore, in situ/operando techniques (e.g., XRD, TEM, Extended X-ray absorption fine structure (EXAFS), fourier transform infrared spectroscopy (FTIR), Raman) and computational chemistry (e.g., theoretical calculations, molecular dynamics modeling) are required to be carried out, which can not only assess the precise nature of the active sites and identify the intermediate species to reveal the reaction pathways, but also determine the key parameters of designing efficient catalysts for highly efficient CO₂ conversion. Machine learning is the practice of building models from data, which has attracted intensive attention in catalysis, which has been integrated into the computational and experimental research in recent years. It can analyze the atomistic potentials and predict the catalytic properties of the catalytic systems. For example, DFT has been widely employed as an important tool for potential pathway screening, free energy calculations, the d-band center prediction, and molecular dynamics simulations, thus obtaining effective information about the relevant surface structures and compositions of catalysts under reaction conditions. Accordingly, machine learning provides increased value to advance the catalysis research, which not only helps researchers get more valuable information with existing data but also provides more sophisticated methods to collect new and useful data. Therefore, it can contribute to gain deep insights into the synthetic parameters for efficient catalysts designing and optimal reaction conditions in thermocatalysis, photocatalysis, and photothermocatalysis. In conclusion, comprehensive measures of precise catalyst preparation, in-depth structural characterization, thorough CO₂RR testing, and advanced computational study are indispensable to explore the full potentials of the technologies of thermo-, photo-, and photothermocatalytic CO₂ conversion.

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Conflict of Interest
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