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Green Carbon Science: Scientific Basis for Integrating Carbon Resource Processing, Utilization, and Recycling

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green carbon science

Preface

The general principles of green chemistry guide the design of environmentally benign products and processes. It is known that the efficient utilization of carbon resources and carbon recycling are of great importance for the sustainable development of our society, and there are many related challenging scientific issues to be solved. Herein we attempt a holistic view on carbon resource processing, utilization, and recycling, and we call this "green carbon science". We will discuss the definition and the four key principles of green carbon science and highlight some related fields including petroleum refining, the production of liquid fuels and chemicals from coal and methane, and transformations of CO_2 and biomass into fuels and chemicals.

1. Introduction

Carbon is the fourth most abundant element in the universe, and it is the key element of life on earth.[1] We are made of carbon-containing compounds and also eat carbon-containing compounds.[1] Moreover, if one thinks of fuels and polymers, it is clear that carbon is the basis of our economy, our homes, and our means of transport. One could say: we live in the age of carbon.

The existence of an appropriate amount of CO_2 in nature is absolutely necessary because CO_2 is essential for biomass production. Before the industrial revolution, the concentration of CO_2 in the atmosphere had not changed considerably for a long time. However, the amount of CO_2 has increased continuously since the industrial revolution because of the combustion of huge amounts of fossil fuels (coal, petroleum, and natural gas) and their derivatives. Fossil fuel utilization is based on the exothermic chemical reactions that generate heat and CO_2. It is estimated that the combustion of fossil fuels results in the emission of more than 30 billion tons of CO_2 annually worldwide,[2] which leads to an increase of CO_2 content in the atmosphere and the oceans. Since the dawn of the industrial revolution, the CO_2 concentration in the atmosphere has risen from about 280 ppm to more than 380 ppm in 2009,[3] and is still increasing steadily. The increased concentration of CO_2 may not only influence global climate significantly, but also result in a pronounced change in our ecosystem because some plant species are more sensitive to the CO_2 concentration than others.

Nowadays, most fuels and energy used are derived from fossil resources, and fossil energy will continue to be the dominant energy source in the foreseeable future, which will lead to further net emission of CO_2. On the one hand, we cannot obtain enough alternative resources to replace fossil resources in the near future. On the other hand, the existing fossil fuel reserves are limited and are being gradually depleted, while our demand of energy is increasing continuously. Therefore, mankind faces the carbon conundrum: the environmentally harmful effects caused by the excessive formation of atmospheric CO_2 and the diminishing of fossil fuel resources.[2] Sustainable development is one of the most important issues for humans and is a great challenge. Chemically, feasible and effective solutions to the problem are the efficient use of the limited fossil resources and the development of processes to convert biomass and CO_2 into fuels and value-added chemicals on a large scale.

Green chemistry, which is the design of chemical products and processes that reduce or eliminate the use or generation of hazardous substances,[4] has received extensive attention and has become firmly entrenched in academia and industry.[5] Green chemistry started in the early 1990s, and the origins and history have been discussed in detail by Anastas

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and co-workers.[4] The well-known "Twelve Principles of Green Chemistry" are a categorization of the fundamental approaches taken to achieve the green chemistry goals of benign products and processes.[4] Poliakoff and co-workers provided a condensed version of the 12 principles to form a mnemonic (Scheme 1), which captures the spirit of green chemistry.[5a]

Some other concepts related to green chemistry have also been proposed and discussed. For example, Sheldon suggested the E factor as a metric of greenness,[6] which is defined as the mass ratio of waste to desired product. The waste problem of a chemical process can be readily evaluated quantitatively by the E factor, which motivates the manufacturers to pay as much attention as possible to the elimination of waste and the maximization of raw-material utilization. The E factor has been widely adopted by the fine-chemicals and pharmaceutical industries.[7] A decade ago Anastas and Zimmerman proposed "green engineering" and its 12 principles,[8a] which include the related underlying features of green chemistry described from an engineering viewpoint. These principles are also well accepted,[6b,8b] and Tang et al. suggested more concise statements of the 12 principles.[8b] Obviously, the general principles of green chemistry, green engineering, and the E factor cover all areas of chemistry and related processes.

The efficient utilization of carbon resources, the reduction of carbon emission, and carbon recycling have become a strategic focus and are great challenges for our societies.[2,3,9–12] The processing and utilization of fossil resources,[10] biomass conversion,[11] and the capture and transformation of CO_2[12] have been studied extensively. The significance of the greener use of carbon resources has been emphasized by several scientists. For example, Olah and co-workers discussed an anthropogenic chemical carbon cycle for a sustainable future.[2] We discussed green carbon science in relation with the utilization of fossil energy with low carbon emission.[13] Tour et al. addressed that green use of carbon-based resources minimizes the environmental impact of carbon fuels and could allow a smooth transition from fossil fuels to a sustainable energy economy.[14] Recently, a Green Carbon Center has been created at Rice University, USA,[15] and a Green Carbon Company has been established in New Zealand.[16]

As previously mentioned, the processing and utilization of carbon resources and carbon recycling have been studied extensively, but mostly separately. Our intention in this Essay is to present an integrated discussion of efficient carbon resource processing and utilization and carbon recycling, and summarize the related scientific issues. We discuss green carbon science in Section 2 and four key principles of green carbon science are proposed. Several important fields, including petroleum refining and transformations of coal, methane, CO_2, and biomass into liquid fuels and chemicals are highlighted in Section 3. A succinct outlook is presented for each of the fields on the basis of green carbon science and the collective knowledge and achievements of the scientific community.

P	• Prevent wastes
R	• Renewable materials
O	• Omit derivatization steps
D	• Degradable chemical products
U	• Use safe synthetic methods
C	• Catalytic reagents
T	• Temperature, Pressure ambient
I	• In-Process Monitoring
V	• Very few auxiliary substances
E	• E-factor, maximize conversion of feed into product
L	• Low toxicity of chemical products
Y	• Yes, it is safe

Scheme 1. Condensed principles of green chemistry.

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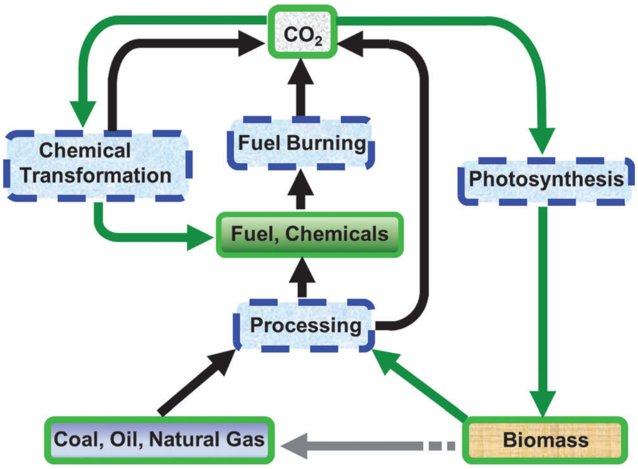

Figure 1. The simplified carbon cycle and related processes.

2. Green Carbon Science

A simplistic carbon cycle relating the utilization of fossil resources, the conversion of biomass, and the recycling of CO_2 is shown in Figure 1. The fossil feedstock is converted into various fuels and chemicals, and CO_2 is released during the feedstock conversion to produce the fuels and chemicals. However, the CO_2 released can be captured and transformed chemically back into fuels or chemicals. Unfortunately, CO_2 is released again in the transformation processes. Meanwhile, plants convert CO_2 into biomass by photosynthesis, and the renewable biomass can be converted into fuels and chemicals and CO_2 is emitted in the process as well. The use of biomass can save the fossil resources and thus reduce the net increase of CO_2 in the atmosphere.

Most of the current processes shown in Figure 1 are not highly efficient. Huge amounts of valuable carbon resources are wasted. The total amount of CO_2 released is much greater than that recycled; in other words, the carbon cycle shown is not achieved because of the tremendous net emission of CO_2. It is ideal to approach the carbon cycle by minimizing the net CO_2 emission, which involves efficient processing and utilization of carbon resources and carbon recycling and deals with many scientific issues. Here we define green carbon science as the study and optimization of the transformation of carbon-containing compounds and the relevant processes involved in the entire carbon cycle from carbon resource processing, carbon energy utilization, CO_2 fixation, and carbon recycling to utilize carbon resources efficiently and minimize net CO_2 emission. Four key principles of green carbon science can be summarized as follows.

1) The reaction $C+O_2 \rightarrow CO_2$ should occur in energy utilization, while it should be minimized in the processes to produce fuels and chemicals.
2) Carbon atom economy should be used as a criterion to evaluate each step of the carbon cycle and should be optimized.
3) Chemical carbon recycling, including efficient CO_2 capture and utilization, should supplement natural carbon recycling.
4) The capability of chemical biomass conversion and utilization should be enhanced to minimize the use of fossil resources; this is equivalent to making use of carbon recycling by combining natural photosynthesis with chemical processes.

3. Important Areas of Green Carbon Science

3.1. Optimization of Petroleum Refining

Transportation fuels play an important role in modern society. The catalytic cracking of petroleum is an important way to produce transportation fuels. In the process, by-products such as coke and dry gas (consisting mainly of hydrogen, methane, ethane, and ethylene) are produced as indicated in Figure 2.

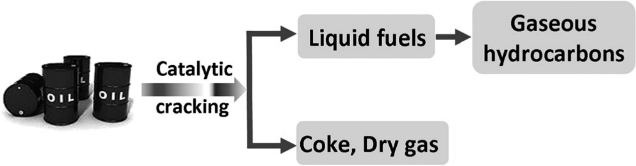

Figure 2. Simplified illustration of the catalytic cracking of petroleum.

The breaking of C–C bonds is the major reaction, which is endothermic and needs energy input.[10a–c] Great effort has been devoted to reducing the energy consumption and CO_2 emission in the processes for the production of liquid fuels. However, on the basis of green carbon science, some scientific and technological issues need to be considered further. Currently, gasoline and diesel are the main transportation fuels. It is known that low-severity cracking of oils can reduce the production of by-products (e.g. coke and dry gas). When gasoline is produced from crude oil, the C–C bonds in the feed molecules are broken to a greater extent, which consumes more energy and feedstock. If diesel is the target product, the extent of C–C bond breaking and the amount of by-products such as coke and dry gas can be decreased. As a result, more crude oil can be converted into the desired product, and energy consumption and CO_2 emission can be reduced in the process. Moreover, diesel engines are already more efficient than gasoline engines (45% efficiency versus 30%), and further advances to 55–63% are possible.[17] Therefore, the efficiency of carbon resource utilization is much higher when diesel is used. At present, gasoline is the dominant target product for catalytic cracking processes in many countries, such as in China.[13] Greater effort should be made to optimize the diesel/gasoline ratio, which will contribute to reducing the carbon imbalance in the carbon cycle of Figure 1. It should be emphasized that optimizing the diesel/gasoline ratio is a complex issue. Besides carbon utilization efficiency, some other factors must be considered, such as the cost for replacing existing transportation vehicles and the control of particulate matter emission.

A significant portion of the feedstock is inevitably converted into coke in the catalytic cracking of crude oils.[10a–c,18,19] The cokes reduce the activity and selectivity of the catalysts significantly; this reduces the catalytic cracking efficiency, wastes the feedstock, and releases more CO_2. As a result, the cokes must be removed so that the catalysts can be regenerated. There are five main types of cokes identified in catalytic cracking: catalytic coke (from condensation and dehydrogenation reactions), catalyst-to-oil coke (catalyst-to-oil coke is a result of the hydrocarbons entrained within the spent catalyst as it enters the regenerator), thermal coke (formed by a free radical mechanism), additive coke (identical to Conradson coke), and contaminant coke (caused by the catalytic dehydrogenation activity of the deleterious FCC feed metals e.g. Ni, V, and Fe).[18] Catalysis is crucial to reduce the coke formation and enhance the carbon atom efficiency of the reactions. In recent years, some new zeolites with macro-, meso-, and micropores matched by ordered acidic sites have been designed and prepared.[20] These zeolites have potential applications in catalytic cracking processes with higher atom efficiency.

At present, the coke produced in the catalytic cracking process is burned off to regenerate the catalyst, and regeneration in fluid catalytic cracking (FCC) units is one of the major CO_2 producers in the petroleum refinery. The heat produced by the combustion of the coke is used in various ways,[18] such as heating the feed to the reaction temperature and providing energy for the endothermic cracking reactions. It is known that coke can be used to produce syngas ($H_2 + CO$). Therefore, a reasonable way to use the coke more efficiently is to produce syngas in the regeneration of the catalysts, instead of producing CO_2; in other words, catalyst regeneration and syngas production would be integrated, and some research has been carried out on this.[19] The current catalyst regenerator and the cracking catalysts should be modified in order to achieve this goal, that is, the catalyst regenerator should serve in both catalyst regeneration and coke gasification. In the 1980s, Min and co-workers at the Research Institute of Petrochem Processing, SINOPEC (China), performed some experiments to test this integration in the oil refining facility in Shijiazhuang (China), but the process was not commercialized.[13]

3.2. Transformation of Coal

Coal is one of the major energy sources and its abundance worldwide is considerably greater than that of oil and natural gas.[10e] Coal is a mixture consisting mainly of aromatic macromolecules containing heteroelements (e.g. O, S, N). Presently, coal is used mainly by direct combustion to generate heat. Coal can also be used as a feedstock to produce carbon-based materials, liquid fuels, and value-added organic chemicals by what can be classified mainly as direct and indirect routes[10e,21] (Figure 3).

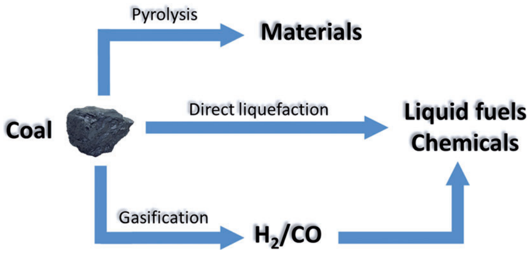

Figure 3. Routes for coal transformation.

In the direct route, coal macromolecules are broken down into lower-molecular-weight compounds that can be further refined into clean liquid fuel and used to produce a variety of chemicals by removing the heteroatoms.[10d,e,21c] Hydrogen is required to increase the H/C ratio of the products. Usually, a series of steps are involved for producing transportation fuels and chemicals, such as coal dissolution, reduction of molecular size to allow access to catalyst pores, removal of heteroatoms, hydrogenation of aromatic rings and opening of the saturated rings, further reduction of the molecular size, and increase of the H/C atomic ratio.[10e] In general, the catalysts in the processes should accelerate these reactions. Different transition-metal-based catalysts,[22] acid catalysts,[23] and metal halides[24] have been used to catalyze the reactions. Iodoboranes and iodine could be used as homogeneous catalysts to hydrogenate high-grade bituminous coals, resulting in an increase of the aliphatic compounds at the expense of the aromatic structures of these coals.[25] Although much effort has been devoted to optimizing the operation conditions in different steps, such as the pretreatment of coal, catalytic hydrogenation of the treated coal, and separation of the products,[10d,e,26] the direct route is still more expensive than petroleum-based processes. Because of the extremely complex and variable chemical and physical properties of coal, it is very difficult to control the carbon bond transformations in the liquefaction process. Much attention should be paid to this because it is crucial for the further development of this technology. Besides for the production of liquid fuels and chemicals, coal can also be used as a raw material for preparing higher-value materials, such as metallurgical cokes, activated carbons, molecular sieving carbons, graphites, carbon fibers, humic acid based materials, and coal/polymer, which has been reviewed.[21d]

In indirect coal liquefaction, coal is first transformed into syngas by breaking all of the C–C bonds in the macromolecules by reaction with oxygen and steam. Then the syngas is converted into fuels and chemicals, such as gasoline, diesel, arenes, alkenes, alcohols, dimethyl ether, aldehydes, carboxylic acids, and carboxylic esters by corresponding chemical routes.[10f,27] Gasoline and diesel, for example, can be derived by the Fischer–Tropsch synthesis. Numerous catalysts have been developed using different active components (e.g., Fe, Co, Ru, Pt), supports (e.g., SiO_2, Al_2O_3, mesoporous materials, zeolites, carbon nanofibers, carbon nanotubes), and promoters (e.g., transition-metal oxides, rare-earth oxides).[10f,28] The activity of the catalysts and their selectivity to the desired products depend strongly on both the composition and the structure of the catalysts. The different possible combinations of active components, supports, and promoters provides many opportunities to achieve this goal.[10f,28] The carbon efficiency of the indirect process is low because stoichiometrically about 50% of the carbon is converted into CO_2.[21c] The carbon efficiency can be higher if fuels and chemicals with high O/C ratios, such as alcohols, dimethyl ether, aldehydes, carboxylic acids, and carboxylic esters, are synthesized from syngas. A notable example is the synthesis of ethylene glycol by CO reduction and coupling reactions.[29]

3.3. Transformation of Methane

Methane is an abundant resource, which can be used as a fuel directly. It exists as natural gas and in the ocean as methane hydrate. In addition, methane is also naturally generated by biosystems and can also be produced from biomass by biotechnology and biomass technology—this can be considered as "renewable methane".[30] Efficient utilization of methane is an important issue, which also contributes to achieving the carbon cycle in Figure 1. A number of indirect and direct (Figure 4) strategies have been explored for the conversion of methane to more-useful fuels and chemicals.[30–32]

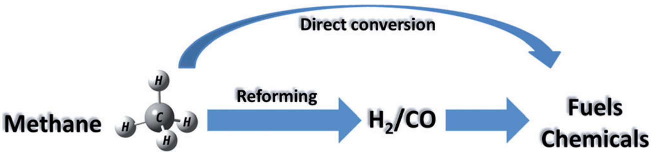

Figure 4. Indirect and direct routes to methane conversion.

In the indirect route, methane is first converted into syngas. The direct routes involve processes such as selective oxidation, high-temperature coupling, and two-step methane homologation to produce a variety of valuable chemicals (e.g., methanol, formaldehyde, higher hydrocarbons, acetic acid, acetone).[30–32] Methane can also be used in aromatization reactions.[33] In the next part of this section we will briefly discuss methane reforming to produce syngas and the selective oxidation to methanol, which are among the most important protocols for the transformation of methane into high-quality fuels and chemicals.

Syngas production from methane includes processes like steam reforming, CO_2 reforming, oxygen reforming, and a combination of these.[32] Steam reforming, which is based on the reaction of methane with water, was commercialized more than 80 years ago,[32,34] and is widely used. A Ni-based catalyst catalyzes the reaction effectively,[35] especially in the presence of promoters such as B, La, and Rh.[35a] Rh catalysts supported on ZrO_2, CeO_2, $Ce_xZr_{1-x}O_2$ and SiO_2 are very efficient for the reaction and the size of the Rh nanoparticles has a significant influence on the activity and stability of the catalysts.[35b]

The reaction of methane and CO_2 is referred to as CO_2 reforming or dry reforming of methane. In recent years, much effort has been invested in this reaction, especially for the exploitation of the catalysts. Nickel- and noble-metal-based catalysts have been widely studied.[36] The reaction catalyzed by $Ni/CeO_2–ZrO_2$,[37a] and Ni/MgO[37b] had high methane and CO_2 conversions. Mesoporous $Ni/CaO–ZrO_2$ nanocomposites with high thermal stability were prepared, which exhibited excellent catalytic performance for the reaction.[38a] However, noble-metal catalysts are usually more efficient. It was also reported that trace amounts of a Pt dopant in the Ni-based catalyst could enhance the stability of the catalyst effectively for the CO_2 reforming of methane.[38b] $Pt/ZrO_2–SiO_2$ was a very active and stable catalyst,[39a] and the activity of a Rh catalyst was more than two orders of magnitude higher than that of a Ni–Cr catalyst.[39b] A study of 2011 indicated that a $CoCeZrO_x$ catalyst could be used to catalyze the reaction, and addition of Mn enhanced the catalytic activity and stability of the catalyst remarkably.[39c] The main advantage of the CO_2 reforming of methane is the consumption of two greenhouse gases.[32,40]

The reaction of methane with oxygen is referred to as the oxygen reforming or the oxidative reforming of methane. From an energy efficiency point of view, the oxygen reforming of methane is very promising because it is thermodynamically favorable, and high methane conversion can be achieved at high space velocities.[32] Noble-metal-based catalysts,[41] non-noble-metal-based catalysts,[42] and multimetallic catalysts[43] have been investigated for the reaction, and some excellent results have been obtained. For instance, a simple Ni/MgO catalyst exhibited reasonable activity and satisfactory syngas selectivity.[44] Using Pt and Rh supported on alumina as the catalysts, high methane conversion and selectivity for H_2 and CO could be achieved at very short reactor residence times.[45]

These three basic reforming routes can be integrated in combined reforming processes, such as oxygen–steam reforming, oxygen–CO_2 reforming, and oxygen–steam–CO_2 reforming.[32] Coupled reforming processes have some obvious advantages. For example, a combined process can be more energy-efficient than the individual reforming reactions because the heat generated by the exothermic reactions can be used by the endothermic reactions.[46] It was found that $NiCoMgCeO_x/SZ5564$ could be used as the catalyst in oxygen–steam reforming,[47] and high methane conversion with an excellent syngas selectivity was obtained at thermoneutral conditions. $Pt/ZrO_2–Al_2O_3$ was an efficient catalyst with high stability in the oxygen–steam and oxygen–CO_2 reforming processes.[48a] A Ni/Al_2O_3 catalyst manifested good activity and stability for the oxygen–CO_2 reforming, and the addition of oxygen reduced coke formation on the catalyst surface.[48b] Noble-metal-modified Ni catalysts showed excellent performance owing to the synergetic effect of the metals. The activity, stability, hot-spot, and regeneration properties could be improved.[48c] However, much attention should be paid to safety issues when oxygen exists in the reaction system.[49]

As a fuel and an important chemical feedstock, methanol is used on a large scale.[50] Nowadays, methanol is synthesized mainly from syngas, which is produced primarily from coal or natural gas. Such a two-step approach has high capital and operation costs and high energy consumption and CO_2 emission. The selective oxidation of methane to methanol is a promising route in terms of both carbon atom efficiency and the efficient utilization of natural gas, and chemical catalysis,[51] biocatalysis,[52] and photocatalysis[30,53] have all been utilized to promote the reaction. For example, the aerobic oxidation of methane to methanol in water under mild reaction conditions was reported using a bipyrimidinyl platinum–polyoxometalate hybrid complex supported on silica as the catalyst.[51a] The reaction products were mainly methanol and formaldehyde with about 1% methane conversion. A solid catalyst for the direct low-temperature oxidation of methane to methanol was developed,[31a] which had satisfactory activity and stability, but it was extremely difficult to achieve high methane conversion and methanol selectivity simultaneously. Using methane monooxygenases from methanotrophic bacteria as the catalysts, the controlled oxidation of methane to methanol under ambient conditions could be achieved.[52a] Recently, a chemical strategy for tuning the catalytic profile of the monooxygenase P450 MB3 was reported, which simply required the addition of an appropriate chemically inert perfluoro fatty acid to the enzyme catalyst, and the catalytic system was effective in catalyzing the oxidation of methane to methanol using O_2 as the oxidant.[52b] Photocatalytic methods have also been used for methane conversion.[53] Using water as the oxidant, methane could be transformed into methanol by photocatalysis with a WO_3 catalyst doped with lanthanum at atmospheric pressure and 370 K.[54a] The reaction also took place at room temperature in water using visible light and a WO_3 catalyst,[54b] and the products observed were mainly methanol, O_2, and CO_2.

3.4. Transformation of CO_2

The recycling of CO_2 is a key feature of the carbon cycle in Figure 1. CO_2 is the major greenhouse gas. It is also an abundant, nontoxic, nonflammable, easily available, and renewable carbon source. Besides the production of syngas by the reaction with methane (CO_2 reforming of methane) as discussed in Section 3.3, CO_2 can be used as a feedstock to synthesize fuels and synthetic products through the formation of various chemical bonds, including C−C, C−O, C−H, and C−N bonds;[12] some typical transformations are shown in Figure 5. Some routes have been used in industry, such as the production of urea, salicylic acid, cyclic carbonates, and polypropylene carbonate.[12] In this section we will discuss the transformations of CO_2 into cyclic carbonates, copolymers, methanol, formic acid, and dimethyl carbonate (DMC).

Cyclic carbonates have wide applications as polar aprotic solvents, precursors for polycarbonate materials, and intermediates in organic synthesis. The cycloaddition of CO_2 with epoxides to produce five-membered cyclic carbonates is one of the most successful routes to utilize CO_2 and is used in industry.[12a] Many catalysts have been developed for this cycloaddition reaction, such as alkali-metal salts,[55a] transition-metal complexes,[55b] functional polymers,[55c] quaternary ammonium and phosphonium salts,[55d] and ionic liquids.[55e,f] Alkali-metal salts are among the most promising catalysts for this reaction because they are cheap, abundant, nontoxic, and easily recyclable. However, the activity of alkali-metal salts is usually low. It is known that co-catalysts can be added to enhance the activity of alkali-metal-salt catalysts, and crown ether,[56a] PPh_3 and phenol,[56b]and cellulose[56c] were found to be very effective co-catalysts. CO_2 can also be used as a building block for producing valuable biodegradable copolymers.[57] For example, the coupling of CO_2 and epoxides can produce polycarbonates with many outstanding properties, and Salen–metal complexes were proved to be very effective catalysts for these reactions.[57]

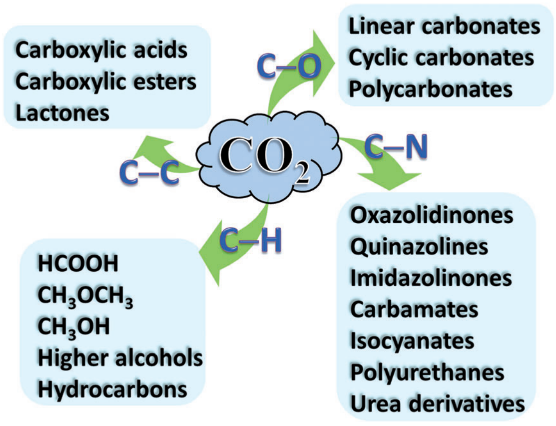

Figure 5. Typical transformations of CO_2.

There are many advantages of using methanol as a fuel and feedstock for the synthesis of hydrocarbons and products currently obtained from petroleum.[58] Methanol is generally manufactured from carbon monoxide and hydrogen produced from coal and natural gas. In the past decades, the hydrogenation of CO_2 to methanol has attracted much attention as an alternative way.[12a–d] Both heterogeneous and homogeneous catalysts have been applied.[59] It was reported that a Cu/ZnO-based catalyst could catalyze the reaction effectively.[59a] The shape of ZnO in the Cu/ZnO-based catalyst had a significant effect on the selectivity for methanol: platelike ZnO nanocrystals showed higher selectivity than rod-shaped ZnO crystals.[59b] When ZnO rods/CdSe of controlled morphology were used as the model support for Cu, a high selectivity towards methanol was realized.[59c] The addition of oxide materials such as Al_2O_3, TiO_2, Ga_2O_3, and MgO could improve the activity and stability of the Cu/ZnO-based catalyst.[60] It was also reported that a nickel catalyst had a higher turnover frequency than a related copper catalyst because the hydrogenation barrier on Ni is remarkably smaller than that on Cu.[61] It was also showed that a ruthenium–phosphine complex could catalyze the hydrogenation of CO_2 to methanol under relatively mild reaction conditions.[59d] In addition to the development of more efficient, cheap, and recyclable catalysts, the production of cheap hydrogen using renewable energy is a key factor for the large-scale application of this route. The photocatalytic reduction of water to H_2, especially with visible light, has been a subject of intense study[62] and has great potential to produce renewable H_2.

Formic acid is a well-known chemical with various uses. Currently, most of the industrial processes to produce formic acid require toxic carbon monoxide or syngas.[63] The formation of formic acid from H_2 and CO_2 is an atom-efficient route, but it is thermodynamically an uphill reaction. The reaction can be shifted towards the product side by the addition of bases.[64] Homogeneous catalysts have been widely studied for this reaction, especially using rhodium,[65] ruthenium,[66] and iridium[67] complexes with various ligands. Heterogeneous catalysts fabricated by immobilizing ruthenium on silica and polystyrene resin were also reported to be active for the reaction.[68] Different amines are commonly used as the bases to overcome the thermodynamic limitation of the reaction.[66c] Recently, basic ionic liquids were used to shift the reaction.[69] In the reaction, Ruthenium immobilized on silica was used as a heterogeneous catalyst, which was dispersed in an ionic liquid aqueous solution. This catalytic system had satisfactory activity and high selectivity. The advantage of this approach was that the formic acid could be recovered easily and both the ionic liquid and catalyst could be reused after a simple separation process. Recently, it was reported that a titania-supported gold catalyst could promote the CO_2 hydrogenation in the presence of neat NEt_3 to form $HCOOH/NEt_3$ adducts effectively.[70] The adducts could be split into pure HCOOH and neat NEt_3 with the help of the high-boiling amine $(n\text{-}C_6H_{13})_3N$. Very recently, a process that allows the continuous hydrogenation of CO_2 to pure formic acid in a single process unit was demonstrated; this was achieved through the integrated design and development of the macroscale process, the mesoscale separation strategy, and the molecular-scale catalyst system.[71] Although the catalytic hydrogenation of CO_2 to formic acid has been extensively studied, its viability on an industrial scale is still unproven. The development of efficient and recyclable catalysts and the economic separation of the product are critical for the commercialization of this route. Similarly, cheap and renewable hydrogen is required for large-scale application.

Dimethyl carbonate (DMC) is a green intermediate in organic synthesis and a useful solvent. Conventionally, DMC is synthesized using methanol and toxic phosgene. Therefore, its synthesis from CO_2 and methanol directly is very attractive. However, the equilibrium conversion of the reaction is very low due to thermodynamic limitations. In order to promote the reaction, it is necessary to remove the produced water using dehydrating agents. Therefore, both dehydration to shift the reaction and efficient catalysts are necessary for the reaction. To date, homogenous catalysts, including cobalt, nickel, niobium, and tin complexes, have been used to catalyze the reaction.[72] Zirconium-, vanadium-, copper-, cerium-, tin-, titanium-, and potassium-based catalysts have been used for the reaction.[73-75] Dehydration agents used were ketals,[74a] orthoesters,[74b] and molecular sieves.[74a,75] It was demonstrated that the reaction under supercritical condition was also favorable to producing the product.[75] It should be emphasized that this route has not been industrialized. The problems may be solved by the combination of designing highly efficient catalysts and dehydration agents, and separating DMC and water produced in the reaction process.

The use of solar energy to convert CO_2 into valuable organic compounds can achieve negative CO_2 emission. Therefore, this route can contribute to approaching the carbon cycle shown in Figure 1. The photocatalytic reduction of CO_2 to valuable chemicals such as methanol and formic acid has been studied by many researchers. Semiconductors (e.g. TiO_2 and CdS) proved to be effective photocatalysts.[76] The photocatalytic reduction of CO_2 generated methanol, formic acid, and formaldehyde in the presence of photosensitive semiconductor powders suspended in water under the irradiation of light with wavelengths shorter than 500 nm.[76a] Methanol and methane were formed from CO_2 reduction with H_2O under UV irradiation using TiO_2 and the TiO_2/Y-zeolite catalysts.[77] In order to use visible light effectively, different strategies, such as the use of dye sensitization, were developed to extend the absorption of the photocatalysts into the visible region.[78] It was reported that NiO–$InTaO_4$ catalysts could reduce CO_2 to methanol under visible-light illumination. The methanol yield increased with the amount of NiO cocatalyst.[79]

A few years ago, CO_2 was photocatalytically reduced with H_2O to produce methanol, ethylene, and methane in a steady-state optical-fiber reactor under artificial light and real sunlight irradiation using a dye-sensitized Cu–Fe/P25 photocatalyst.[80] The main advantage here was that the optical fibers could transmit light uniformly throughout the reactor. In addition, the processing capacity of the reactor was higher because the photocatalyst could be dispersed on the optical fibers with large surface area. It was also reported that functionalized carbon nanoparticles with gold or platinum coating were effective photocatalysts for the reduction of CO_2 in aqueous solution under visible-light irradiation, and formic acid was produced with an estimated quantum yield of about 0.3 %.[81] Very recently, the photocatalytic reduction of CO_2 to $HCOO^-$ under visible-light irradiation was realized over a photoactive Ti-containing metal–organic framework (MOF).[82] This type of MOF material has a high density of immobilized Ti sites within its pores. While the photocatalytic conversion of CO_2 into valuable hydrocarbons is very promising and has been widely investigated, some key problems need to be solved for the development of an economically viable technology, such as designing highly efficient catalysts and reactors.

3.5. Transformation of Biomass

The fossil resources are diminishing worldwide because they are not renewable. At the same time, nature produces a huge amount of biomass each year, but only about 4% is currently utilized by humans.[11a] Among the various sustainable energy options only biomass is a source of carbon-based fuels and chemicals.[83] Conversion of biomass into fuels and chemicals is an effective way to liberate us from the reliance on fossil resources, and can also be considered as recycling of CO_2 by combination of photosynthesis and chemical methods. Therefore, it is crucial in the carbon cycle of Figure 1. The interest in the conversion of biomass to fuels, chemicals, and materials increased sharply during the last ten years within academia and industry.[84] Starch, triglycerides, and lignocellulose are the main classes of feedstock derived from biomass, and numerous bioproducts can be manufactured from them;[11] this is shown schematically in Figure 6, and is addressed briefly below.

The use of starches and triglycerides as starting materials to produce bioethanol and biodiesel has been commercialized.[11c] Starch feedstocks comprise glucose polysaccharides joined by α-glycosidic linkages, which are easily hydrolyzed

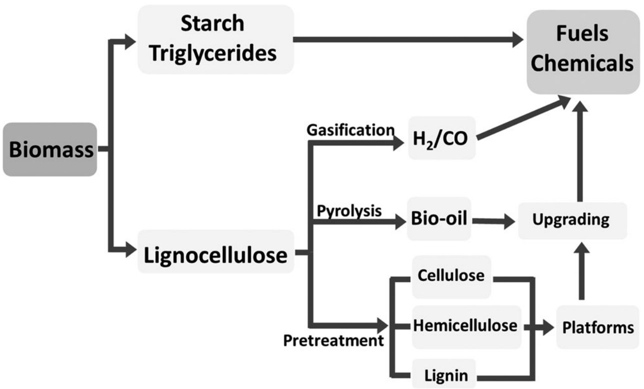

Figure 6. Possible ways from biomass to fuels and chemicals.

into the constituent sugar monomers, making them easy to transform into bioproducts.[11c,83] Large starch biorefineries established decades ago have been processing million tons per year of corn, wheat, and potato starch to produce different products using biocatalysts and chemocatalysts.[11f] Large amounts of bioethanol, in particular, are produced from starch-based feedstocks. Triglyceride feedstocks are derived from various vegetable oils, waste oil products, algae, and animal fat.[85] Biodiesels can be produced from triglycerides and methanol by transesterification.[86] In general, three categories of catalysts are used for biodiesel production: alkalies,[87] acids,[88] and enzymes.[89] Recently, some new routes have been developed. For example, biodiesel was produced from methanol under supercritical conditions and catalyst was not required.[90]

Lignocellulosic biomass is composed mainly of cellulose, hemicellulose, and lignin, which is much more abundant and non-edible. Different approaches have been studied to use lignocellulosic biomass as the feedstock to produce biofuels and chemicals; these can be classified as thermochemical and hydrolysis-based routes. The thermochemical transformation of lignocellulosic feedstocks into fuels and chemicals can be divided into gasification and pyrolysis processes.[91] In principle, thermochemical methods can transform all the organic matter in lignocellulose into upgradeable platforms (e.g. syngas and bio-oils). In the gasification route, lignocellulosic biomass is first converted into syngas, which is then used as the raw material to produce liquid fuels and chemicals by catalytic reactions such as the Fischer–Tropsch synthesis.[10f,28,92] The main advantage of gasification is that it is suitable for any lignocellulosic feedstock. However, the process requires high temperatures and purification of the syngas.[93] In the pyrolysis process, the lignocellulose is also treated at elevated temperature in the absence of oxygen or in the presence of much less oxygen than required for complete combustion. The bio-oil generated is a complex mixture containing alcohols, aldehydes, ketones, acids, esters, and aromatic compounds.[11f] This route has been reported to provide up to 70% yield of bio-oil based on the initial feedstock.[94]

In general, short residence times are required for the production of bio-oils, and the properties of the bio-oils depend both on the specific starting feedstock and the conversion conditions.[95] The pyrolysis protocol allows for the total utilization of lignocellulosic biomass, and can also be used for processing lignin after the extraction of carbohydrates from lignocellulosic biomass.[95,96] However, the bio-oil product cannot be utilized directly in internal combustion engines currently used because of its high acidity and oxygenate content, which leads to corrosion and low energy density, respectively.[97] Oxygen-removal procedures are necessary to get high-quality liquid fuels and value-added chemicals. Catalytic hydrodeoxygenation, zeolite upgrading, and ketonic decarboxylation have been used to upgrade the bio-oils.[97,98]

In the hydrolysis-based routes to convert lignocellulosic feedstock into bioproducts, the feedstock is first separated into carbohydrates and lignin, which are then used as starting materials for producing fuels and chemicals by biological or chemical pathways. The main advantages of the hydrolysis-based method is that the reaction can be carried out under milder conditions and allows for better control of conversion selectivity.[97]

The use of inedible carbohydrates (e.g. cellulose and hemicellulose) from biomass as feedstocks to produce biofuels or biochemicals is highly desirable because the feedstocks are abundant and cheap, and use of these feedstocks will not affect the food supply. The carbohydrates can be transformed into bioproducts through biological or chemical processes. For example, bioethanol, biobutanol, and biohydrocarbons can be produced from cellulose by fermentation.[83,97] In typical processes, C_5 and C_6 sugars are first produced by hydrolysis of cellulose and are further fermented to bioethanol or biobutanol or to other commodity chemicals. In recent years, extensive research has been performed on this interesting topic.[99] However, there are still technical and economic impediments to developing inexpensive commercial processes. Cheaper sources of carbohydrates, improving the efficiency of the fermenation, and reducing the cost of the enzymes are all important for reducing the cost of the bioproducts.

The carbohydrates can also be transformed into fuel and chemicals by different catalytic reactions such as oxidation, dehydration, and hydrogenation. The oxidation of carbohydrates can produce many valuable chemicals.[100] For example, the selective oxidation of glucose, the most abundant monosaccharide in nature, can produce gluconic acid, which is widely used in the pharmaceutical and food industry; this biotechnological process has been industrialized.[11f,100] The chemocatalytic oxidation of glucose to gluconic acid on Pt and Pd catalysts has been studied extensively using oxygen as the oxidant, and bismuth could be used as a co-catalyst to improve the catalytic efficiency of platinum.[101] The aerobic oxidation of glucose to gluconic acid catalyzed by supported Au catalysts in aqueous solutions achieved excellent activity and selectivity.[102] An alumina support doped with basic metal oxides such as sodium oxide and calcium oxide could enhance the activity of the Au/Al_2O_3 catalyst considerably.[102b] It was also demonstrated that the metals in Au–Pd and Au–Pt particles acted synergistically to promote the reaction.[103]

The hydrogenation of carbohydrates can produce sugar alcohols, which are widely used in the food industry and are also precursors in the synthesis of fuels and value-added compounds.[100] One of the most produced sugar alcohols, sorbitol, with an estimated worldwide production of 700 000 tons per year, is produced by the catalytic hydrogenation of glucose.[11f] Ni-based catalysts, particularly Raney nickel, are commonly used for the industrial-scale production of sugar alcohols.[104] Nevertheless, the stability of the Ni-based catalysts is not high because of the leaching of the nickel. Ruthenium-, cobalt-, platinum-, palladium-, and rhodium-based catalysts have also been used for the hydrogenation. For example, supported Ru[105a] and Pt[105b] catalysts showed satisfactory performance for the conversion of cellulose to hexitols. Ru immobilized on different supports was used for the hydrogenation of glucose and cellobiose, and high yields of the corresponding polyol products were obtained.[106] The direct conversion of cellulose into ethylene glycol in high yield was achieved on a supported tungsten–carbide catalyst;[107] this provides a novel route to ethylene glycol. A recent study indicates that controllable conversion of cellulose into ethylene glycol, propylene glycol, and sorbitol could be accomplished using a Ru/C catalyst in the presence of WO_3.[108] In particular, propylene glycol, an important commodity chemical, could be obtained directly from cellulose with a yield of more than 30%. Besides improving the catalytic efficiency of the reactions, a crucial aspect for the production of fuels and chemicals by the hydrogenation of carbohydrates is to minimize the consumption of hydrogen from external sources; currently the hydrogen is derived mainly from fossil sources.[97]

The production of fuels and chemicals from biomass via platform compounds is very attractive. The dehydration of carbohydrates leads to the formation of important biomass-derived platform molecules such as 5-hydroxymethylfurfural (5-HMF) and furfural (2-furaldehyde), which are versatile and valuable intermediates for plastics, pharmaceuticals, fine chemicals, and liquid fuels.[109] Considerable efforts have been devoted to the transformation of carbohydrates such as fructose,[110] sucrose,[111] and inulin[112] into 5-HMF in different solvents under acidic conditions. The conversion of glucose or cellulose into 5-HMF is more difficult. Progress has been made in this area few years ago, and high yields of 5-HMF were obtained in different solvents with metal chloride salts (e.g. $CrCl_3$, $SnCl_4$, $AlCl_3$) as the catalysts.[113] Some other important reactions, such as the production of 2,5-dimethylfuran from fructose[114] and glucose[115] and furfural from xylose,[113d,116] have also been studied using different catalysts.

Lignin is one of the main constituents of lignocellulosic biomass, which is the richest source of aromatic hydrocarbon compounds in nature,[11a] and is a byproduct in the pulp and paper industry. Lignin is a three-dimensionally amorphous polymer consisting of methoxylated phenylpropane structures.[11b] It is challenging to break lignin down chemically into useful fragments in profitable ways. There are very few reports of efficient ways of recovering such aromatic products. The only notable commercial process has been the production of vanillin from lignosulfonates, a by-product of the sulfite pulping industry.[11h] Although in the past the utilization of lignin has received less attention than the use of carbohydrates, it is receiving increasing attention.[11b,117] Lignin can be converted into syngas by gasification, and syngas is then transformed into liquid fuels and various chemicals, as indicated above. Besides for the production of syngas, lignin can also be used for the production of many very useful chemicals by cracking or hydrolysis, reduction, or oxidation.

Lignin can be broken into low-molecular-weight compounds by cracking reactions, and these intermediates are further converted into valuable products; HZSM-5 was found to be a very effective catalyst for the cracking reactions.[118] In the lignin reduction, lignin or lignin subunits are converted into simple aromatic compounds such as phenol, benzene, toluene, and xylene by hydrogenation and hydrodeoxygenation over various transition-metal-based heterogeneous catalysts[113d,119a] and homogeneous catalysts like nickel complexes.[119b] The aromatic compounds can then be transformed into bulk and fine chemicals using the methods already developed in the petroleum industry. Lignin oxidation reactions utilize oxygen or H_2O_2 to form platform chemicals or target aromatic chemicals with additional functionality.[11b] Different catalysts have been used in these oxidations; these include Pd/Al_2O_3,[120a] $Cu\text{-}Mn/Al_2O_3$, and $Cu\text{-}Ni\text{-}Ce/Al_2O_3$,[120b] Co(salen)/SBA-15[120c] heterogeneous catalysts, and Co,[121a] Fe,[121a] Cu,[121b] and V[121b,c] complexes. It was also demonstrated that ruthenium[122a] and vanadium[122b] complexes could catalyze the depolymerization of lignin model compounds by cleavage of the aryl ether C−O bond, and the reactions were redox-neutral. With its unique structure and chemical properties, lignin has great potential as a carbon resource for the sustainable production of fuels and a wide variety of bulk and fine chemicals. However, controlled lignin depolymerization and separation processes are rather difficult and the problems have not been properly solved.

4. Summary and Outlook

Sustainable development is a great challenge for our society. Improving the efficiency of carbon resource utilization and carbon recycling can contribute significantly to meeting this challenge. As shown in Figure 1, highly efficient transformations and utilization of fossil reserves, biomass, and CO_2 with minimized energy consumption and CO_2 emission are all essential. Many processes used today require improvement and new approaches should be explored and developed through interdisciplinary research in chemistry, material science, process engineering, and environmental science.

The highly efficient utilization of the limited petroleum resources is extremely important because in the near future we have no other alternative sources and technologies to provide the tremendous amount of liquid transportation fuels we need.[10a–c] Designing catalysts and developing the processes to minimize the generation of coke, CO_2, and dry gas under industrial conditions are still critical issues. As discussed in Section 3.1, there is potential to use petroleum more efficiently with less CO_2 emission by optimizing the diesel/gasoline ratio and integrating catalyst regeneration and syngas production. In order to produce more diesel, catalysts and process technologies are needed, which selectively break the C−C bonds in the heavy components in the catalytic cracking of oil. In addition, the main products from the catalyst regenerator should be CO and H_2 instead of CO_2 and H_2O. The novel regenerator may be designed as a multistage system, and the cracking catalysts should be effective not only for the cracking reactions, but also for the generation of syngas.[18]

The direct combustion to generate heat and electric power will continue to be the dominant use of coal in the foreseeable future. However, with the depletion of oil, the production of liquid fuels, chemicals, and materials from coal will become increasingly important. Both direct and indirect routes for this purpose have obvious advantages and disadvantages.[10e] In principle, the carbon efficiency of the direct process can be high, but the process is very complex and molecular hydrogen is required.[21] In addition, the efficiency of the process depends strongly on the rank and the chemical structure of the coal used. The indirect route is more versatile, but the C–C bonds in the coal macromolecules are broken down completely with more energy consumption.[21c] Both direct and indirect coal liquefaction routes are technically feasible. However, current technologies are energy-intensive and the efficiency must be improved further. The development of highly efficient and cheap catalysts, and the design of the corresponding reactors and separation facilities should be combined to reach this goal. In addition, much more attention should be paid to the development of new reactions and processes that produce new chemicals, intermediates, and materials based on the unique structure of coal with the least degree of carbon–carbon bond cleavage.[21d]

The effective conversion of methane into high-quality liquid fuels and value-added chemicals remains a great challenge. The reforming of methane to generate syngas, which is then processed by other chemical routes, is a feasible way. Steam and CO_2 reforming processes to generate syngas are endothermic, and thus the processes are highly energy-intensive, and they require high temperatures; this leads to less energy efficiency along with some other problems, such as the fast deactivation of the catalysts, and high capital and operation costs.[42a] Much attention should be paid to oxygen reforming and the combined reforming processes including oxygen–steam reforming, oxygen–CO_2 reforming, and oxygen–steam–CO_2 reforming because they can be energetically efficient, and are thermodynamically favorable even at lower temperatures. The combined reforming processes, in particular, couple the endothermic reaction and the exothermic reaction, and the H_2/CO ratio of the product can be manipulated by more operational parameters.[32,46] However, some challenging problems remain, such as the high local temperature on the surface of the catalysts, the formation of coke, and the difficulty in controlling the operation conditions. Besides, thermal balance and safety issues of the processes should be considered more carefully because of the existence of oxygen in the reaction systems.[49] Special attention should be paid to develop catalysts that are active at lower temperatures for the combined reforming processes, such that the problems originating from high operation temperature can be avoided.

The selective oxidation of methane to produce more valuable fuels and chemicals such as methanol is another challenging task of great importance because methane is a very stable molecule with high C–H bond energy. It is extremely difficult to achieve high methane conversion and methanol selectivity simultaneously.[51] Up to now, the approaches are not feasible for large-scale application due to the low efficiency and/or the low yield of the desired product. Understanding the mechanism of selective C–H bond activation and designing highly active, selective, and stable catalysts at mild conditions are very important for developing the commercialized technology. The photocatalytic production of fuels and chemicals from methane and water is a promising route that can proceed beyond thermodynamic limitations and the reaction can be carried out under mild conditions. However, most of the reported photocatalytic methane conversion reactions give a low product yield and low energy efficiency still far away from our requirements.[30,53] The development of potent photocatalysts and the design of novel photocatalytic reactors are crucial aspects for developing economically competitive processes. Special attention should be paid to using visible light.

The conversion of CO_2 into fuels and chemicals is challenging in terms of both thermodynamics and kinetics.[9,12] The number of valuable and spontaneous reactions of CO_2 with one other chemical (two-molecule reactions) is very limited because of the low energy level of CO_2. Strategies have to be developed to solve this thermodynamic problem.[69] An effective way is to seek the reactions in which CO_2 reacts with two or more compounds simultaneously. This methodology provides more opportunities to find new thermodynamically favorable reactions and may open ways to produce chemicals using CO_2 as a building block. Thermodynamic studies and catalyst design should be combined to explore the new reactions. Another way to overcome the thermodynamic barrier for CO_2 reactions is to use solar energy, which is one of the best solutions to the CO_2 problem. However, at present the energy efficiency and yields of the desired products are too low to be economically viable, and much more work needs to be carried out to enhance the efficiency of the existing routes and to explore new reactions.[76] Similarly, use of electric energy can also break the thermodynamic limitation for CO_2 conversion reactions, but for most of the electrochemical reactions, the low efficiency remains a problem. In addition, at present the large-scale application of electrochemical approaches is limited by the availability of enough cheap and renewable electricity. From the kinetic point of view, the activation of CO_2 is also a bottleneck in CO_2 utilization.[12,59] It should be noted that a CO_2 conversion process does not necessarily reduce the total amount of CO_2 if the reaction is highly energy-intensive and/or the efficiency of the process is not high enough. To approach the carbon cycle in Figure 1, we must continue to explore highly efficient CO_2 transformation reactions and industrial processes.

Biomass provides us a huge amount of renewable carbon source. Efficient transformation of biomass into high-quality fuels and chemicals is a long-standing task. Production of transportation fuels using starch and triglyceride is technologically easier than using lignocellulosic biomass and has been commercialized, but the sources of these feedstocks are very limited compared with the amount needed. In addition, use of these resources for fuel and chemical production competes with their present use in the food supply.[97] Hence, abundant and cheap lignocellulosic biomass feedstocks should be used. Energy input is required when transforming lignocellulosic feedstocks due to their high molecular weight and complex structures.[98] Therefore, their conversion may not get net energy and make contribution to reduce the total amount of CO_2 if the efficiency of the conversion processes is low. Many current routes are technically feasible, but economically prohibitive and need to be further improved to achieve efficient and low-energy-consumption processes on large scale. On the other hand, the unique structure of lignocellulosic biomass offers excellent opportunity to design and produce new chemicals.[11] Special attention should be paid to exploring novel strategies that produce products with desired properties, in which the structures of the feedstocks are retained as much as possible. In this way, we can get the products required with less energy consumption. It can be expected that not only more industrial processes for converting biomass into chemical products that are the same or similar to those derived from fossil reserves will be developed, but also many new valuable products from biomass, which are currently not produced from fossil resources, will be produced in the future.

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