

Review

Analysis of Research Status of CO₂ Conversion Technology Based on Bibliometrics

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Abstract: The concentration of carbon dioxide in the air has risen sharply due to the use of fossil fuels, causing environmental problems such as the greenhouse effect, which seriously threatens humans' living environment. Reducing carbon dioxide emissions while addressing energy shortages requires the conversion of CO₂ into high added-value products. In this paper, the status of CO₂ conversion research in the past ten years is analyzed using the bibliometric method; the influence of countries and institutions, journal article statistics and other aspects are statistically analyzed, and the research status of carbon dioxide catalytic conversion is briefly introduced. Finally, according to the analysis results and the existing problems of CO₂ catalytic conversion research, the future development direction of CO₂ catalytic conversion research is prospected.

Keywords: CO₂; conversion; bibliometrics; photocatalysis; electrocatalysis; plasma catalysis

1. Introduction

Due to the burning of fossil fuels, the large amount of CO₂ in the atmosphere has exceeded the natural carbon cycle. The resulting series of global environmental climate problems seriously imperils human existence and ecological environment [1]. It is an important challenge, but also an opportunity, for humans to convert CO₂ into value-added chemicals and fuels, not only for dealing with climate change, but also for reducing humans' dependence on fossil energy. The survey has shown that the demand for oil, coal, natural gas and their derivatives will be maintained for a long time in the future, especially with the increasing population; the demand for carbon-based fuels, plastics and drugs will also increase [2]. In order to meet humans' demand for carbon-based products, the concept of green development has been accepted more and more, so researchers have a strong interest in converting CO₂ into high value-added products.

However, the conversion of CO₂ into other high value-added products requires a high energy input, because of the highly symmetrical structure of CO₂ and the highest oxidation state of carbon. So far, CO₂ is mainly converted into C₁ compounds (methane, methanol, formic acid, etc.), C₂ compound (ethane, acetic acid, ethanol, formate, etc.), cyclic carbonate, dimethyl carbonate, carbonate, decanoate, salicylic acid and other chemical products through catalytic conversion [3], electrochemical conversion [4], enzymatic conversion [5], plasma conversion [6], and bioconversion [7].

Bibliometrics plays an important role in evaluating the research value of a certain field and predicting development directions. At present, bibliometric methods have been applied in many fields,

such as balkanized research in ecological engineering [8], the study of mycobacterium chimera [9], drug repurposing [10], and so on. However, in the field of CO₂ conversion, few scholars use bibliometric methods for analysis. To fill this gap, this article carries out data processing for relevant research articles on CO₂ conversion through the bibliometric method, makes a reasonable analysis of the current research trend of CO₂ conversion based on the processing results, and looks forward to the future research prospects.

2. Results and Discussion

2.1. Publication Outputs

Based on the number of articles published annually, the research hotspot changes in this field can be understood briefly and the future development trend of the field can be predicted. As shown in Figure 1, both the total number of articles and the number of research English articles have increased over time. The number of research articles in English increased from 51 in 2010 to 798 in 2019, which is enough to show that research on CO₂ conversion is gaining popularity year by year. It is worth mentioning that the number of articles on CO₂ conversion research in 2017 (622 articles) was a sharp increase from 2016 (441 articles), which may be because the CO₂ content in the atmosphere reached a historical high at that time in 2016, and the formal entry into force of the Paris Climate Agreement has further accelerated the research process. Therefore, it can be predicted that the research intensity in this field will continue to increase in the next few years.

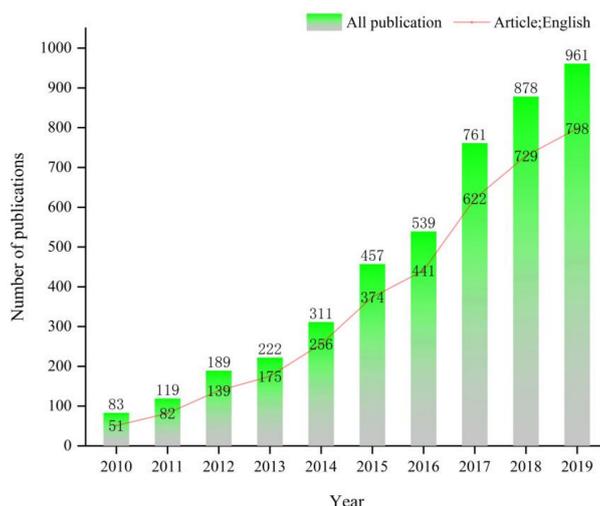


Figure 1. Annual number of publications from 2010 to 2019.

2.2. Journal Analysis

Impact factor (IF) is the most common standard for evaluating the influence of journals. In the same field, the higher the IF value of journals is, the stronger influence and greater reading value journals will have [11]. In addition, the h-index, proposed by Hirsch in 2005 to reflect the influence of the author, is widely accepted and gradually applied to evaluate the influence of countries, institutions and journals [12]. In this paper, the h-index of countries and journals are calculated, based on the filtered data for indicating the influence of countries and journals in the field of CO₂ conversion research.

The 3670 screened articles were published in 481 journals, among which 1401 articles were separate subjects and the remaining 2269 were interdisciplinary. The articles are grouped based on the IF value that was published by the Journal Citation Report (JCR) in 2019, and there were 59 articles published in $0.1 \leq \text{IF}_{2018} < 1$ journals; 2886 articles published in $1 \leq \text{IF}_{2018} < 10$ journals; 690 articles in the $10 \leq \text{IF}_{2018}$ journals. Besides, there are 35 journals not evaluated in JCR 2019.

Table 1 lists the top ten journals in the volume of publications. It can be seen that in the top ten journals, Applied Catalysis B: Environmental and Angewandte Chemie: International Edition has higher impact factors and h-index values, indicating that the two journals have higher impact in this field. The journal with the largest number of articles (214) is Journal of CO₂ Utilization, but the journal has a lower h-index of only 33.

Table 1. The performance of the 10 most popular journals.

Journal	TP	IF	h-Index	Percentage
Journal of CO ₂ Utilization	214	5.189	33	5.83%
Applied Catalysis B: Environmental	148	14.229	205	4.03%
ACS Catalysis	112	12.221	139	3.05%
International Journal of Hydrogen Energy	103	4.084	187	2.81%
Journal of Materials Chemistry A	85	10.733	152	2.32%
Chemsuschem	83	7.804	130	2.26%
Angewandte Chemie: International Edition	79	12.257	482	2.15%
Catalysis Science & Technology	72	5.726	86	1.96%
Chemical Engineering Journal	62	8.355	172	1.69%
RSC Advances	61	3.049	113	1.66%

Note: TP = the number of publications, IF = impact factor (published by the JCR in 2019).

2.3. Country/Region Analysis

The analysis of country/regional publications provides a simple understanding of the contribution and influence of a country/region in the field of study [13]. The 3670 selected articles involved 74 countries/regions, of which 2750 (74.93%) were completed in separate countries, and 762 (27.71%) articles were completed jointly by two countries. The most collaborative articles were completed by six countries, and there was only one (0.13%) article like this.

Figure 2 shows the relationship between the output of the top ten countries and their h-index. Since 25.07% of the articles have an international cooperative relationship, the actual national participation of 3679 articles is 4784. As we can see, both China and the United States have higher publications and h-indexes than other countries. It is worth noting that, although China (1465, 30.62%) has a higher volume of publications than the United States (671, 14.03%), the h-index is not much different (79:77). That is to say, although China pays much attention to CO₂ conversion research and plays a leading role in this field, the research depth needs to be improved. It is also worth mentioning that the two countries of Japan (204, 4.26%), and Spain (117, 2.45%) have a small amount of publications, but have a higher h-index than countries that publish in the same range.

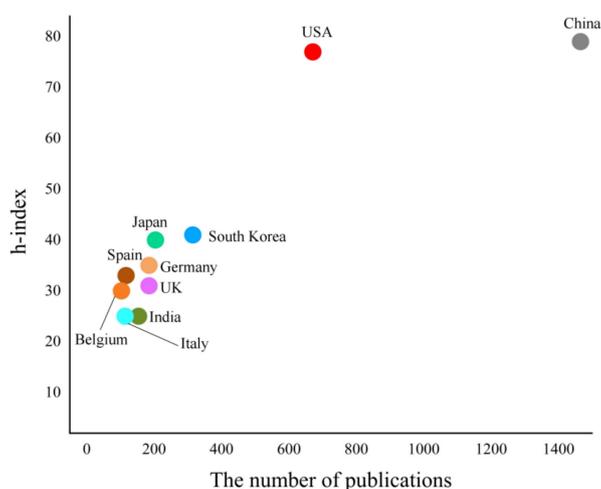


Figure 2. The performance of the top 10 representative countries (TP > 103).

2.4. Institution Analysis

Factors such as the volume of publications and cooperation between institutions in the field of analytical research can determine the influence of each institution. A total of 2074 institutions are involved in the selected data, but 1160 (55.93%) of the institutions appeared only once. Among the 3670 articles, 1077 (29.35%) were completed by a single institution, and the most collaborative article was one (0.02%) with a total of 10 cooperative institutions. Figure 3 is a network diagram of the cooperation between 75 institutions with a number of occurrences higher than 10. The different colors represent different institutions from different continents, and the most frequently occurring institution in Asia is the Chinese Academy of Sciences (283). The largest number of occurrences in the Americas was Penn State University (37); the most frequent occurrence in Europe was University of Antwerp (51).

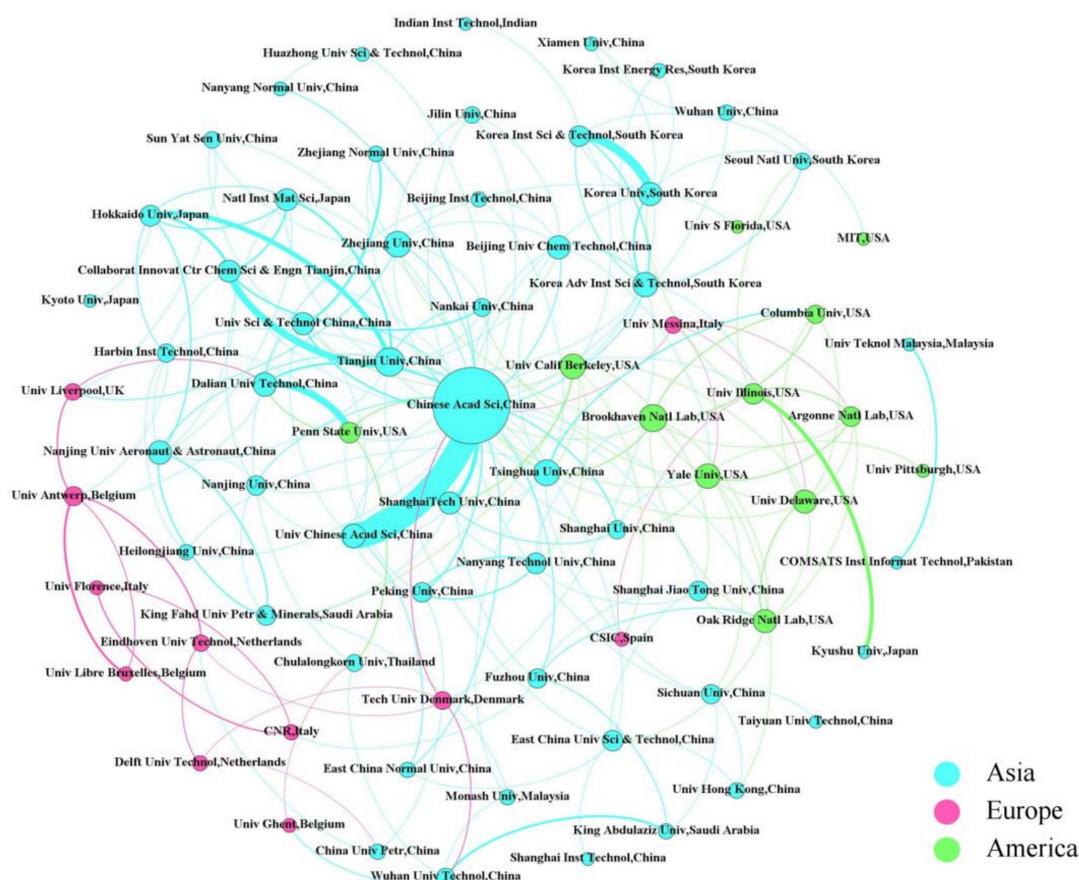


Figure 3. The collaboration network of 75 institutions (TP > 10).

It can be clearly seen from the diagram that the number of institutions from Asia is the largest, up to 52, accounting for 69.33% of 75 institutions. This means that Asia pays much more attention to CO₂ conversion than other continents. At the same time, it can be clearly seen from Figure 3 that the Chinese Academy of Sciences plays a leading role in this field, and its partners mainly focus on Asian institutions; it also has direct cooperation with some institutions in the Americas and Europe.

Table 2 lists the top ten institutions with a large number of documents (TP > 30), using the volume of publications and h-index to indicate the influence of the top ten institutions in the field of CO₂ conversion. It can be seen from the table that the Chinese Academy of Sciences is superior to other institutions, both in terms of the volume of publications and h-index, which indicates that the Chinese Academy of Sciences has a high degree of attention in this field and has a certain influence in this field. In addition, the top ten organizations in this issue come from three different countries, including six institutions from China, which further confirms the fact that China has high concern and influence in this field.

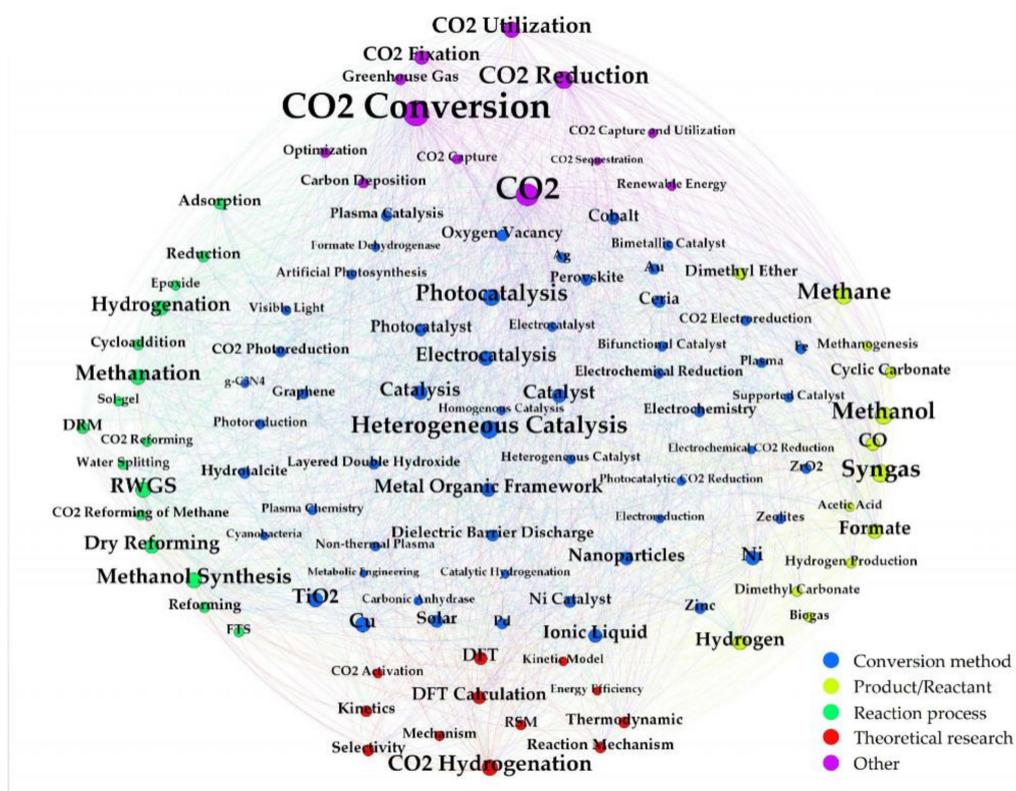
Table 2. Top ten institutions with a large number of documents (TP > 39).

Institution	TP	h-Index	Country	Percentage
Chinese Academy of Sciences	283	35	China	3.91%
University of Chinese Academy of Sciences	118	18	China	1.63%
Tianjin University	71	29	China	0.98%
Dalian University of Technology	69	16	China	0.95%
Korea Advanced Institute of Science and Technology	58	17	South Korea	0.80%
Nankai University	55	17	China	0.76%
Korea University	53	13	South Korea	0.73%
University of Antwerp	51	20	Belgium	0.70%
University of Science and Technology of China	45	17	China	0.62%
Korea Institute of Science and Technology	39	15	South Korea	0.54%

2.5. Research Topic Analysis

Among the filtered articles, there are 1037 (28.26%) articles without author keywords, and nearly 21.50% (223/1037) of the articles were published in 2019. Therefore, it is not scientifically rigorous to analyze the research trends in the field of CO₂ conversion research based on author keywords. At the same time, since different authors have individualized differences in the expression of the same noun, keywords with different expressions of the same meaning need to be combined.

As shown in Figure 4, the keywords after screening and classification can be divided into five categories: CO₂ conversion mode, reaction process, product/reactant, theoretical research and other CO₂ related keywords. It can be seen from the figure that during the decade of 2010-2019, the conversion mode of CO₂ roughly divides into catalytic conversion, direct electrochemical reduction conversion, biotransformation, enzymatic conversion, plasma conversion, etc.

**Figure 4.** Classification map of the top 108 keywords (Frequency > 10).

2.6. Catalytic Conversion

For CO₂ conversion, the most-studied technology is catalytic conversion technology, and this conclusion can be clearly seen from Figure 4. In this method, technologies such as photocatalysis, electrocatalysis, plasma catalysis, and conventional thermal catalysis are widely studied. The mechanism, catalyst systems and prospect of these methods will be introduced briefly in this article.

2.6.1. Photocatalytic

The photocatalytic reduction of CO₂ is achieved by simulating photosynthesis of plants. The essence is that semiconductor photocatalysts generate photo-generated electron-hole pairs under light conditions, and promote the oxidation-reduction reaction between CO₂ and H₂O to generate hydrocarbons. Figure 5 is a schematic diagram of hydrocarbons produced by the photocatalytic reduction of CO₂ [14]. In the process of photocatalytic reaction, when the energy of light radiation is higher than its own forbidden band width, the electrons will be excited to transition from the valence band to the conduction band, thereby forming holes having oxidizing ability and electrons having the reducing ability required for catalytic reaction. Subsequently, the electrons react with H₂O to reduce CO₂ to hydrocarbons such as methanol, methane, formaldehyde, and formic acid; while photo-generated holes with strong oxidation ability oxidize H₂O to release O₂. Catalysts are essential for photocatalytic processes. Here are three photocatalyst materials used commonly: semiconductor materials, graphene-based nanomaterials and MOFs-based heterogeneous catalysts.

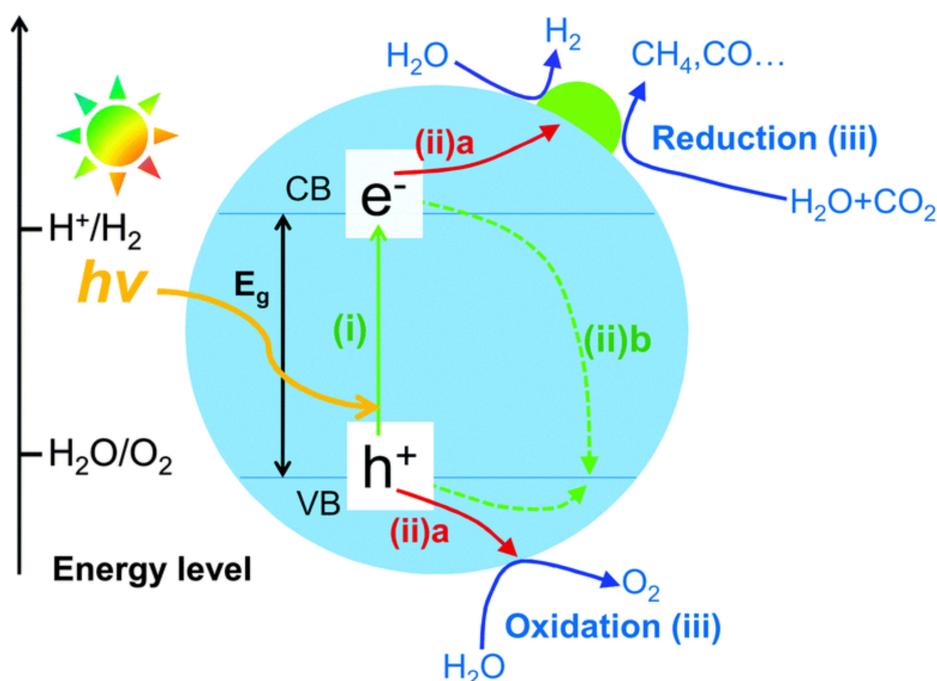


Figure 5. Schematic illustration of the basic mechanism of photocatalytic reduction of CO₂ with H₂O on a semiconductor photocatalyst. Adapted and reprinted with permissions from [14], Copyright (2016) Royal Society of Chemistry (RSC).

Photocatalyst systems have been widely studied in three systems: semiconductor materials, graphene composites and metal-organic framework (MOF). Semiconductor materials include many types of inorganic binary compounds, such as TiO₂, ZnO, CdS, SiC, etc. Among them, TiO₂, as a typical semiconductor material, has received more research, due to its high stability and low cost [15,16]. However, the photo-response range of TiO₂ is narrow, the utilization rate of light is extremely low, and photo-generated electron-holes are easily generated. In order to improve the conversion and selectivity of the photocatalytic process, a variety of TiO₂ surface modification methods have been developed,

including doping, metal deposition, alkali modification, heterojunction structure, and the loading of carbon-based materials [17–20].

Graphene or reduced graphene oxide (RGO) has attracted wide attention, due to its unique electronic properties, large theoretical specific surface area and stable chemical properties [21]. Hsu et al. [22] used graphene oxide to efficiently convert CO₂ to methanol. The modified Hummer method was used to synthesize GO photocatalyst, which improved the catalytic activity of the catalyst. The modified graphene oxide converted CO₂ to methanol under visible light irradiation, and the conversion rate was 0.172 μmol · g_{catalyst}⁻¹ · h⁻¹, which was six times higher than that of pure TiO₂. Tan et al. [23] successfully synthesized a new graphene oxide material, GO–OTiO₂, with the highest photoactivity when the GO loading was 5%. After 6 h of reaction, the yield of CH₄ was 1.718 μmol · g_{catalyst}⁻¹ · h⁻¹, which has significantly improved light stability, and maintains 95.8% reactivity, even after six hours of light exposure. Liu et al. [24] prepared TiO₂-RGO as a photocatalyst, and the yields of CH₄ and CH₃OH can reach 2.10 μmol · g_{catalyst}⁻¹ · h⁻¹ and 2.20 μmol · g_{catalyst}⁻¹ · h⁻¹, respectively. The rapid transfer from TiO₂ to graphene inhibits photo-generated electron-hole recombination. Takayama et al. [25] prepared a graphene CuGaS₂/RGO/TiO₂ composite material. Since the RGO bridging layer provides an electron channel between CuGaS₂ and TiO₂, it has a high efficiency. The yield of CO is 0.15 μmol · g_{catalyst}⁻¹ · h⁻¹.

MOF is a three-dimensional crystalline microporous material composed of metal oxygen clusters and organic connecting molecules. It has a large surface area and porosity, and has high flexibility in adjusting structure and composition. It is applied in the fields of adsorption, separation and gas storage [26,27]. Generally, the MOF is a structure formed by an organic linker, and the thermal stability of the material is weak, so it must be modified to achieve photochemical activity [28]. Wang et al. [29] reported doping Zr₆O₄(OH)₄(para-biphenyldicarboxylic acid)₆ frameworks (UIO-67MOF) with ligands containing Ir, Re and Ru, in which Re-MOF showed the activity of CO₂ photocatalytic reduction. Subsequently, Fu et al. [30] prepared Ti and amine-functionalized Ti₈O₈(OH)₄(benzene-1,4-dicarboxylate-NH₂)₆ frameworks (NH₂-MIL-125 (Ti)). CO₂ was reduced to HCOO⁻ under visible light irradiation, while MIL-125 (Ti) (MOF without amine functional group) showed only UV activity. In addition, amine functional groups increase the absorption of carbon dioxide, which in turn facilitates the conversion process. Sun et al. [31] prepared amine-functionalized UIO-66 (Zr) MOF. Compared with NH₂-MIL-125 (Ti), the yield of HCOO⁻ in NH₂-UIO-66 (Zr) increased by 1.6 times. Choi et al. [32] synthesized ReI (CO)₃(BPYDC)Cl (BPYDC = 2,2'-bipyridine-5,5'-dicarboxylate) and combined it with UIO-67MOF. By systematically controlling its density in the framework, it was found that Re₃-MOF had the highest photocatalytic activity. Based on the structure and activity of Re-MOFs, coating the surface of Ag nanocubes (Ag / Re₃-MOF) with Re₃-MOF to limit the photoactive Re center to the surface of Ag nanocubes can increase the CO₂ conversion rate by a factor of seven, and has long-term stability under visible light for up to 48 hours.

For the photocatalytic reduction of CO₂, the problems of photo-generated electron-hole recombination and low solar energy utilization still exist. Therefore, the overall conversion and selectivity of photocatalytic reduction of CO₂ need to be improved. At present, a single catalyst system cannot solve these problems well. How to efficiently combine different types of catalysts and work together for the catalytic reduction of CO₂ is still a future development direction in the field of photocatalysis.

2.6.2. Electrocatalysis

Electrocatalytic reduction is a technology that converts CO₂ into carbon monoxide (CO), hydrocarbons, alcohols, esters, carboxylic acids and other new substances, through the cathode and anode in aqueous or non-aqueous solvents [33]. As shown in Table 3, according to the number of electrons transferred, the electrochemical reduction of CO₂ can usually be divided into 2, 4, 6, or 8 electron reactions [34], and due to the small difference in thermodynamic potential energy between several possible reactions, the products obtained are usually mixtures of carbon compounds, such as

nano-metal catalysts, metal-organic frameworks (MOFs), covalent organic frameworks (COFs) and carbon nanomaterials. Nanometal catalysts with high specific surface area and active sites have attracted much attention, including nanowires, nanoparticles, nanotubes, and nanoporous membranes [39–43]. In order to improve the reactivity and selectivity of electroreduction, some scholars have studied alloy catalysts to improve the bonding strength of intermediates on the catalyst surface to improve the reaction kinetics, such as Au-Cu, Ag-Sn, Bi-Cu; the synergy of electronic and geometric effects of bimetals can make the product's Faraday efficiency up to 96.4% [44]. Hollingsworth et al. used super-strong alkaline ionic liquid as an electrolyte and solvent for CO₂ electroreduction, and found that a formic acid product with a Faraday efficiency of 93% was obtained on an Ag electrode, and the reaction potential was only 0.17V [45].

Metal-organic frameworks (MOFs) have attracted increasing attention from researchers, due to their high porosity, large specific surface area, adjustable pore size, and variable functional groups [46]. In addition to hybrid molecular material systems [47–49], some Cu and Zn-based MOFs can also be directly used as electrocatalysts for CO₂ reduction. Hinogami et al. [50] used copper sulfate MOF, with the characteristics of electron conductivity, proton conductivity and uniformly dispersed reaction sites, as a catalyst for CO₂ reduction. Interestingly, copper borate MOF produces only HCOOH products at 1.2V (vs. SHE) potential in aqueous electrolyte, while Cu metal electrodes produce a series of products. In addition, the yield of HCOOH is 13 times that of Cu metal electrodes. Kang et al. [51] deposited Zn-1,3,5-trimellitic acid metal organic framework (Zn-BTCMOF) on carbon paper, as an electrocatalyst for CO₂ reduction in an ionic liquid-based electrolyte system. The morphology of Zn-MOF has a significant effect on the performance. The flaky Zn-MOF shows the highest catalytic activity, due to its large electroactive surface area. By comparing different ionic liquids, it was found that the interaction between fluorine-containing imidazolium ionic liquids and CO₂ was the strongest.

Covalent organic frameworks (COFs) are compounds composed of light elements (H, C, N, O, B, etc.) connected by strong covalent bonds. They belong to a new type of nanoporous polymer composites. The characteristics of high porosity and orderly controllable structure can improve the reactivity and selectivity by changing the chemical structure, and show excellent performance in the adsorption and fixation of CO₂ [52,53]. Lin et al. [54] used COFs to achieve the electrocatalytic reduction of CO₂. Cobalt porphyrin units (TAP) and 1,4-benzaldehyde (BDA) were used as precursor units to successfully prepare two-dimensional COFs materials, which had a 90% conversion rate of CO₂ to CO at 55V potential. Song et al. [55] used cylindrical mesoporous nitrogen-doped carbon nanotubes to directly convert CO₂ to ethanol. At a potential of −0.56V, the Faraday efficiency of ethanol is 77%, and the formation of CO is completely suppressed. The selectivity of ethanol in the CO₂ reduction product was as high as 100%.

Carbon nanomaterials have the advantages of high electrical conductivity, good stability, and low price. They are the most promising catalysts for replacing precious metals for electrochemical reduction. For example, Kumar et al. [56] successfully prepared carbon nanofibers through carbonized polyaniline. This carbon nanomaterial can achieve carbon dioxide reduction under an overpotential of 0.17V, and under the same conditions, it can also obtain a higher current density than Ag nanoparticles. In addition, research has found that heterogeneous atoms, such as nitrogen, boron, sulfur, and phosphorus can improve the catalytic activity and stability of carbon nanomaterials. Among them, nitrogen-doped nanocarbon materials have demonstrated catalytic performance comparable to that of Pt/C electrodes [57,58].

Although electrocatalytic reduction of CO₂ has the advantages of a controllable reaction process, an electrolyte that can be recycled, and a compact reaction system, it also has problems such as relatively slow reaction kinetics and low energy utilization. How to reduce overpotential and improve product selectivity are the main problems facing the electrocatalytic reduction of CO₂. Choosing a more suitable electrode and catalyst may be a breakthrough to solve these problems.

2.6.3. Plasma Catalysis

Plasma is considered to be a fourth material form which is different from solid-liquid-gas. When the temperature of other particles such as ions and gas molecules in the plasma is much lower than the electron temperature, it is called non-thermal plasma (NTP). NTP occurs in the presence of high-energy electrons. It is caused by the inelastic collision between high-energy electrons and CO₂ gas molecules under the action of an electric field. The process is shown in Figure 7. The C=O bond dissociation energy of CO₂ molecules is 5.5eV, and the electron energy in low temperature plasma is mostly between 1–20eV. Therefore, high energy electrons in low temperature plasma can dissociate CO₂ molecules and convert them into CO and O₂. Similarly, plasma can also perform other thermochemically difficult chemical reactions under mild conditions, providing new technical support for traditional chemical reactions [59].

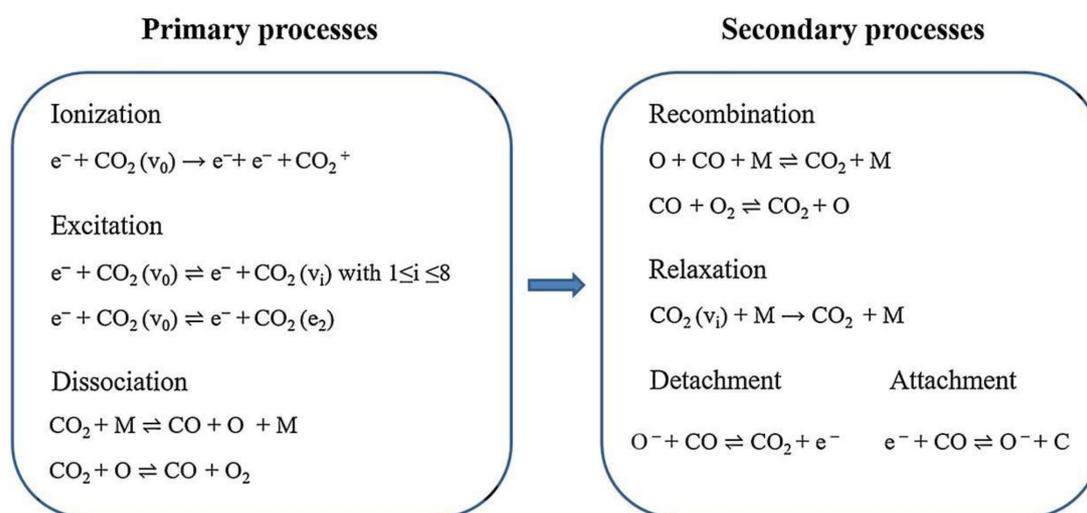


Figure 7. Basic process of CO₂ decomposition in low-temperature plasma (M = CO₂, CO or O₂). Adapted and reprinted with permissions from [59], Copyright 2018, Elsevier.

Low-temperature plasma is a promising CO₂ conversion technology, because it can activate and transform reactive molecules at room temperature, and pressure and reactions are rapid. However, the plasma alone participating in the reaction has low selectivity for the target product, and the conversion rate and energy efficiency need to be improved. The most effective improvement is to add a catalyst in the plasma [60]. The addition of Cu and Mn-supported catalysts to the dielectric barrier discharge plasma can increase the CO₂ conversion rate from 6.7% to 36%, and increase the energy efficiency of the product CO by 116% [61]. Adding a catalyst can also improve the conversion rate and energy efficiency of the DRM reactants. In the process of CO₂-H₂ system conversion using microwave discharge plasma, the addition of Ni / TiO₂ catalyst can increase the CO₂ conversion rate from 14% to 28% [62].

Cryogenic plasma has many advantages not available in other new technologies, including sustainable electrical energy operation at room temperature, great flexibility for materials to be processed, efficient energy storage, low investment and operating costs, and strong applicability. However, the low-temperature plasma technology has a trade-off problem between CO₂ conversion rate and energy efficiency, that is, it is difficult to achieve high CO₂ conversion rate and high energy efficiency at the same time. Studies [63] have shown that this problem may be overcome by improving the plasma system, such as combining plasma discharge with a catalyst, but this requires further research. In addition, by modeling the plasma process, coupling it with other technologies, and further exploring the synergistic effects of plasma-bound catalysts, we can better understand the mechanism of the plasma conversion of CO₂.

2.6.4. Thermal Catalysis

Converting CO₂ into fuel or other value-added products is the ideal way to reduce the continuous emission of carbon dioxide into the atmosphere, and it may be more advantageous to convert to alternative fuels for industrial production or transportation [64]. At present, the fuel products converted by CO₂ catalysis include methane, methanol, formic acid, dimethyl ether, and syngas, etc. [65–68] The transformation of CO₂ to methane is an essential process for the fuel market. Methane is the main component of natural gas, which is easier to transport, handle, and store [69]. By 2030, the CO₂ methanation market is expected to reach 4 to 65 billion cubic meters per year [70]. CO₂ methanation is the most widely studied, and it is mostly conventional thermal catalytic conversion [71]. Therefore, this article mainly introduces the thermal catalytic conversion of CO₂ to methane.

CO₂ methanation refers to the strongly exothermic reaction process of H₂ and CO₂ to form CH₄ and H₂O under the action of 150–500 °C, 0.1–10 MPa, and a metal catalyst [72]. Table 4 lists the main reactions and side reactions performed during the CO₂ methanation reaction. The main reactions in this gaseous catalytic process include reverse water gas shift, CO methanation, reverse dry reforming, and CO₂ methanation. Due to the fact that only the reverse water gas shift reaction absorbs heat, and the other three reactions are highly exothermic, leading to a strong exotherm in the CO₂ methanation process, in order to keep the CO₂ methanation within the ideal temperature range, effective heat dissipation is essential. In addition to temperature problems, side reactions can also cause problems, such as scaling on the catalyst surface, plugging pores, and carbon deposition. In general, the selectivity of the CO₂ methanation reaction depends on the catalyst used and its chemical equilibrium [73].

Table 4. Main reactions and side reactions that occur during CO₂ methanation.

Reaction Equation	$\Delta H_R^{298\text{K}}/\text{kJ}\cdot\text{mol}^{-1}$	Response Type
$\text{CO}_2 + \text{H}_2 \rightleftharpoons \text{CO} + \text{H}_2\text{O}$	41	reverse water gas shift
$\text{CO} + 3\text{H}_2 \rightleftharpoons \text{CH}_4 + \text{H}_2\text{O}$	−206	CO methanation
$2\text{CO} + 2\text{H}_2 \rightleftharpoons \text{CH}_4 + \text{CO}_2$	−247	reverse dry reforming
$\text{CO}_2 + 4\text{H}_2 \rightleftharpoons \text{CH}_4 + 2\text{H}_2\text{O}$	−165	CO ₂ methanation
$2\text{CO} \rightleftharpoons \text{C} + \text{CO}_2$	−172	Boudouard reaction
$\text{CO} + \text{H}_2 \rightleftharpoons \text{C} + \text{H}_2\text{O}$	−131	CO reduction
$\text{CO}_2 + 2\text{H}_2 \rightleftharpoons \text{C} + 2\text{H}_2\text{O}$	−90	CO ₂ reduction
$\text{CH}_4 \rightleftharpoons \text{C} + 2\text{H}_2$	−75	Methane pyrolysis

Through investigation of catalyst performance [74,75], the CO₂ methanation activity of different metals is Ru > Rh > Ni > Fe > Co > Os > Pt > Ir > Mo > Pd > Ag > Au; selectivity is Pd > Pt > Ir > Ni > Rh > Co > Fe > Ru > Mo > Ag > Au. Among them, Ru not only exhibits higher low-temperature catalytic activity but also maintains stability during long-term use. Abe et al. [76] prepared a highly dispersed Ru nanoparticle Ru/TiO₂ catalyst supported by TiO₂ by ion sputtering, and the CH₄ yield reached 100% at 160°C. The carbon dioxide turnover frequency (TOF) of Ru-based catalysts is closely related to the dispersion of active components and the type of support. The dispersion of active components depends on the interaction between Ru and the support. Under the same reaction conditions, the TOF order of Ru catalysts with different supports is Ru/Al₂O₃ > Ru/MgAl₂O₄ > Ru/MgO > Ru/C, and the activity of 15% (mass fraction) Ru/Al₂O₃ catalyst is 10 times higher than that of the Ni-based catalyst [77]. However, the price of metal Ru is high and cannot meet the needs of industrialized large-scale production [78].

In addition to precious metals, transition metals have gradually become an important component of the development of CO₂ methanation catalysts, because of their low cost and availability. Fe-based catalysts were studied earlier and industrialized earlier. Still, the operating conditions are generally high temperature and pressure, which will easily cause the catalyst to deactivate carbon deposits and gradually be replaced by other active metals [79]. Co-based catalysts have relatively low methanation activity and strict requirements on the reaction environment. However, Pt has a better effect on the

performance of Co-based catalysts. Co–Pt catalysts obtained by physical mixing have a carbon dioxide hydrogenation activity that is three times higher than single-metal Co catalysts at low temperatures. This is mainly because H₂ and CO₂ are activated on the surface of Pt particles and Co particles, respectively. The dissociated H is transferred to the surface of the Co particles through the SiO₂ support, followed by a carbon dioxide hydrogenation reaction to generate CH₄. As the distance between Pt and Co nanoparticles increases, the apparent activation energy decreases, obviously [80].

Compared with other transition metals, Ni-based catalysts have higher methanation catalytic activity, and the reaction conditions are relatively easy to control, which has been widely studied [81]. However, Ni-based catalysts have poor thermal conductivity and are prone to sintering and deactivation during the reaction. Therefore, research has mostly focused on improving the sintering resistance of the catalyst. For example, using MgO as a carrier and using the formed MgNiO₂ structural stability to prevent sintering of Ni species [82]; loading the Ni species into carbon nanotubes, using the tube wall to restrict the growth and agglomeration of Ni species, and properly adding Ca ions, will further improve the dispersibility of Ni on carbon nanotubes [83]; strong thermal conductivity, SiC, as a carrier reduces heat accumulation and prevents the high-temperature sintering of Ni species [84]. At the same time, in order to overcome the shortcomings of single active component catalysts in the reaction process, there are also studies of dual active metal or even multiple active metal catalysts for CO₂ methanation, such as the Ni–Ru/Al₂O₃ catalyst prepared by Zhen et al. [85] for the conversion of CO₂ and CH₄ selectivity, which reached 82.7% and 100%, respectively. Although there is much research on Ni-based catalysts, and industrial applications are most likely to be achieved in CO₂ methanation, the current stability is poor. Therefore, it is still necessary to continue the research and development of catalysts to improve catalyst stability while ensuring catalyst activity.

Thermal catalysis has evolved from the addition of catalysts in traditional thermochemical methods and has been put into industrial applications. However, reaction conditions at high temperatures and pressures have limited its development. Therefore, typical thermal catalytic technologies such as CO₂ methanation focus on the development of low-temperature catalysts on the one hand, and the other should pay more attention to the energy replacement and selection and development of high-stability and selective catalysts that meet high-temperature and high-pressure reaction conditions.

3. Materials and Methods

Data sources and processing ideas are shown in Figure 8. Based on the Web of Science SCI-Expanded database, a total of 4740 articles were found on the keywords "conversion of CO₂" or "conversion of carbon dioxide" or "carbon dioxide conversion" or "CO₂ conversion" or "utilization of CO₂" or "utilization of carbon dioxide" or "carbon dioxide utilization" or "CO₂ utilization" and "2010–2019" published. However, the original intention of Web of Science is not to provide accurate data for bibliometrics, so when searching in the form of "topic", all articles with keywords will appear even the keywords in *KeyWords Plus* only. Since *KeyWords Plus* is generated according to the title of the article citation, these articles are not closely related to the topic of the retrieval purpose [86], so these articles should be removed. This paper refers to the "front page" method proposed by Ho et al. [87], to eliminate the articles whose keywords only appear in the *KeyWords Plus*.

In addition, some articles, such as those on the effect of carbonic anhydrase in human body [88–90] and on carbon isotope conversion [91,92], may contain key words in the abstract, but they may not be related to the subject of this study, so they need to be excluded. At the same time, articles that contain retrieval errors such as "...CO₂. Conversion..." [93], "...carbon dioxide. Conversion..." [94] should also be removed.

After the above screening, there are 4552 articles, including 4504 (98.94%) articles in English and 3704 (81.37%) articles in research. For the convenience of analysis, the 3670 (80.63%) English research articles are selected to analyze the basic processing of data in Microsoft Excel 2016. Then, the processed data is imported into Bibexcel for cooperative network and clustering processing, and finally, Gephi is used for data visualization processing.

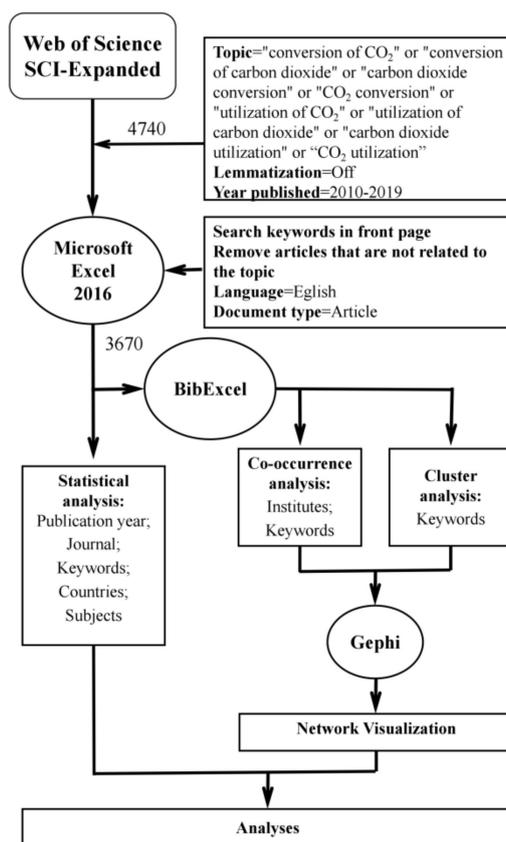


Figure 8. The general flow diagram for systematic bibliometric analyses.

4. Summary and Outlook

In the past decade, research on the conversion of CO₂ into high value-added products has increased year by year, which is attributed to the increasing environmental problems, such as the greenhouse effect caused by CO₂, and on the other hand, concerns about the shortage of energy resources. Therefore, China, the United States and other major countries have played a leading role in the utilization of CO₂ resources, fully reflecting the responsibility and responsibility of the major powers. It must be pointed out that although China has a wide range of research in the field of CO₂ conversion, the overall research level, especially the research on some key theoretical foundations, is weak, so the influence in this field needs to be improved. It is worth noting that, although China's overall level of influence in this field is not outstanding, the Chinese Academy of Sciences is leading the way in many international research institutions, with its strong research team and rich research resources.

By screening and analyzing the keywords, we found that catalytic conversion technology is the most widely studied CO₂ conversion method. Among them, photocatalysis, electrocatalysis, plasma catalysis, and thermal catalysis are the most frequently used methods to reduce CO₂. However, all methods have problems such as high overpotential, low conversion efficiency, and poor product selectivity. Therefore, choosing the type of catalyst has become the top priority, and future research should focus on finding catalysts with multi-electron transport capabilities, improving the selectivity of the product; how to design reaction systems in different media is also the direction of future efforts.

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