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Review on porous nanomaterials for adsorption and photocatalytic conversion of CO₂

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ABSTRACT

Photocatalytic conversion of “greenhouse gas” CO₂ is considered to be one of the most effective ways to alleviate current energy and environmental problems without additional energy consumption and pollutant emission. The performance of many traditional semiconductor photocatalysts is not efficient enough to satisfy the requirements of practical applications because of their limited specific surface area and low CO₂ adsorption capacity. Therefore, the exploration of photocatalysts with high CO₂ uptake is significant in the field of CO₂ conversion. Recently the porous materials appeared to be a kind of superior candidate for enriching the CO₂ molecules on the surface of photocatalysts for catalytic conversion. This paper first summarizes the advances in the development of nanoporous adsorbents for CO₂ capture. Three main classes of porous materials are considered: inorganic porous materials, metal organic frameworks, and microporous organic polymers. Based on systematic research on CO₂ uptake, we then highlight the recent progress in these porous-material-based photocatalysts for CO₂ conversion. Benefiting from the improved CO₂ uptake capacity, the porous-material-based photocatalysts exhibited remarkably enhanced efficiency in the reduction of CO₂ to chemical fuels, such as CO, CH₄, and CH₃OH. Based on reported recent achievements, we predict a trend of development in multifunctional materials with both high adsorption capability and photocatalytic performance for CO₂ utilization.

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1. Introduction

Today, the increasing emission amounts of the “greenhouse gas” CO₂ in the atmosphere by the excessive consumption of fossil fuels (Fig. 1) have given rise to two serious problems: a shortage of usable energy and global climate warming [1]. Making full use of this natural CO₂-rich source by fixing and transforming it cannot only alleviate the greenhouse effect but also generate chemical fuels for carbon resource recycling. In addition to the capture and storage technique, CO₂ conversion appears to be an attractive solution to the energy and envi-

ronmental problems [2]. There are many CO₂ conversion methods, such as plasma reduction [3], biotransformation [4], thermal-assisted catalysis [5], electrocatalytic reduction, and photocatalytic reduction [6–8]. However, because CO₂ is an inert and thermodynamically stable molecule, which requires high energy input for the activation and conversion processes, most CO₂ conversion techniques are potentially energy consuming.

Photocatalysis emerged as an economical technology for CO₂ conversion because it utilizes solar energy to trigger the photochemical reduction of CO₂ to produce hydrocarbon fuels.

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Fig. 1. The changes of annual CO₂ emission and global mean surface temperature from 1990 to 2016 [1].

Compared with other methods, the photocatalytic conversion of CO₂ can be performed under mild temperature and pressure [9–11]. Although the application prospect in this area is very broad, the current efficiency of photocatalysts toward CO₂ adsorption and conversion remains very low, which is the biggest obstacle for the transformation of carbonaceous resources. Therefore, the design and synthesis of high-performance photocatalysts is the key to this technology. The performance of many traditional semiconductor photocatalysts is not efficient enough to satisfy the requirements for their practical applications because of their limited specific surface area and low CO₂ adsorption capacity [12–14]. For the specificity of the CO₂ reduction reaction, an ideal photocatalytic material should possess strong CO₂ adsorption capacity and high catalytic activity. Porous materials have attracted extensive research interest in the CO₂ adsorption field because of their well-developed pore structure and high specific surface area [15]. The advantages of different porous materials in CO₂ adsorption are summarized in Table 1. Upon introducing porous materials with high CO₂ uptake into the photocatalytic system, the CO₂ molecules can be adsorbed and enriched on the surface of the photocatalyst for catalytic conversion. In this regard, the development of multifunctional materials exhibiting both high CO₂ uptake and photocatalytic performance is one of the most promising directions for the photocatalytic conversion of CO₂.

2. Porous materials for CO₂ adsorption

The methods of CO₂ capture include physical adsorption, chemical adsorption, membrane separation, among others. Because of van der Waals forces, the adsorbent surface is covered by a single layer or multi-layer of the molecular adsorbent (Fig. 2(a)), which is characterized as physical adsorption. Chemical adsorption is a process involving the exchange and transfer of valence electrons between the molecular adsorbent and atoms (molecules) on the surface of the adsorbent to form a chemical bond (Fig. 2(b)). Fig. 2(c) presents a schematic diagram of a membrane-separation process [32]. In general, the feed stream is provided at the high-pressure side, whereas the permeate stream flows out at the low-pressure side with the retentate adsorbing on the membrane. In this work, we only focused on solid porous adsorbents for the physical adsorption of CO₂ molecules. In addition, the microcosmic mechanism of the competitive adsorption behavior between CO₂ and CH₄ on the surface of carbon models was investigated using density functional theory (DFT) calculations [33]. The results indicated that the adsorption of the injected CO₂ promoted the desorption of CH₄, thus visually proving the effectiveness of CO₂-ECMB (enhanced coal-bed methane), which was beneficial in trapping CO₂.

The adsorption method, which relies mainly on porous materials with a high specific surface area for CO₂ adsorption, has been the subject of extensive research and application in the field of CO₂ capture. The physical adsorption method is based on the intermolecular attraction between the target molecules and the surface active sites of the porous solid adsorbent. A series of porous solid adsorbents for physical adsorption emerged in the fields of CO₂ adsorption and separation. There are three typical categories of adsorbent porous materials: inorganic porous materials (IPMs), metal organic frameworks (MOFs), and microporous organic polymer (MOPs). The CO₂ adsorption capacity and selectivity as well as the resistance to water vapor mostly depend on the physical characteristics and surface chemical properties of the porous materials. The latest research progress in the area of high-performance porous materials for CO₂ adsorption is reviewed with reference to the material structure parameters and performance.

Table 1

Advantages and disadvantages of adsorbent porous materials.

Solid adsorbent	Advantages	Disadvantages	Ref.
Porous carbon	Various precursors; low cost; light weight; acid and alkali resistance; high thermal-/photo-stability	Poor selectivity; poor water resistance; unsuitable for high pressure adsorption	[16–18]
Molecular sieves	Uniform pore size; definite skeleton structure; high porosity; high thermal-/photo-stability	Poor water resistance; unsuitable for high pressure adsorption; instability under acid or alkali condition	[19,20]
Mesoporous silicon	Well-developed pore structure; adjustable pore size; high thermal-/photo-stability	Poor selectivity; unsuitable for high pressure adsorption; instability under acid or alkali condition	[21–24]
MOFs	Metal-containing active sites; large specific surface area; adjustable micropore size; artificially directional synthesis; designable surface property	Complicated synthesis; high cost; low adsorption capacity under low pressure; instability under acid or alkali condition	[25–28]
MOPs	Small density; large specific surface area; adjustable micropore size; artificially directional synthesis; designable surface property; a certain acid and alkali resistance	Low adsorption capacity under low pressure; poor thermal-/photo-instability	[29,30]

Fig. 2. (a) Physical adsorption and diffusion in nanoporous materials; (b) Schematic diagram of surface species for the chemical adsorption of CO₂ on TiO₂ and/or CeO₂ surfaces (Copyright permission from Elsevier, Ref. [31]); (c) Scheme of simplified membrane gas-separation system such that P₁ is feed (or retentate) pressure and P₂ is permeate pressure (Copyright permission from Annual Reviews, Ref. [32]).

2.1. Inorganic porous materials

2.1.1. Porous carbon materials

Carbon materials, including activated carbon, carbon fiber, and carbon nanotubes, are excellent adsorbent materials. Their high specific surface area and well-developed porous structures enable these materials to be applied in complex environments (such as acids, alkalis, and water vapor) and play an important role in the field of gas adsorption/separation. To date, many types of porous carbons have been well commercialized in gas adsorption/separation systems, including for CO₂ capture. For example, Silvestre-Albero et al. [34] reported petroleum pitch super activated carbon (VR-5 and VR-93) prepared by a chemical activation method using KOH as an activating agent. At 25 °C and 50 bar, the volume adsorption capacity can be as high as 380 and 500 cm³/cm³, respectively. Therefore, the adsorption capacity of CO₂ and other gases on this type of material under high-pressure conditions is very large. Shen et al. [35] prepared a series of porous carbon fibers using a pre-oxidation-chemical activation method with carbon fiber as the raw material. The CO₂ adsorption test indicated that the adsorption capacity was only 4.4 mmol/g at 25 °C and 1 bar. Therefore, the primary problem is how to improve the low partial pressure adsorption capacity and separation selectivity of this material toward CO₂/N₂.

To improve the low-pressure adsorption capacity and selectivity of the activated carbon materials, the researchers introduced nitrogen-containing groups to enhance the affinity for CO₂ based on the molecular structure of CO₂ (electron distribution, polarity) to improve the adsorption capacity and selectivity under low-partial-pressure conditions. It is reported that polyethylenimine (PEI)-derived activated carbon having various nitrogen functional groups and rich nitrogen content possessed typical microporosity with a high specific surface area. The CO₂ uptake at 1 bar was 4.9–5.7 mmol/g at 0 °C and 2.9–3.7 mmol/g at 25 °C. The PEI-derived carbons also exhibited good stability during multi-cycle adsorption–desorption tests and a high selectivity of CO₂ over N₂ at 25 °C [36].

2.1.2. Molecular sieves

Both natural and synthetic molecular sieves such as zeolites are among the most widely investigated adsorbents for CO₂ adsorption [37]. The adsorption of CO₂ on molecular sieves is characterized as physical adsorption. The adsorption capacity decreases rapidly with increasing temperature. In addition, the zeolite adsorbent, which has strong water absorption and low gas selectivity properties, is particularly sensitive to water vapor. Thus, unmodified zeolites are only suitable for anhydrous environments, which limits their industrial application.

With the aim of individuating adsorbing materials with better performance, considerable attention has been paid to the effect of surface modifications on increasing the CO₂ adsorption capacity. The adsorption of CO₂ on the zeolite after modification changed from physical adsorption to chemical adsorption, which improved not only the adsorption capacity of CO₂ but also the water resistance and the selectivity against N₂. Because amine-based chemical absorption is one of the most commonly used techniques for CO₂ removal in industry, several studies have explored the integration of organic amines into porous supports for CO₂ adsorption. The functionalization of zeolites with amines was reported by Su et al. [38], who used a Y-type zeolite with a Si/Al molar ratio of 60 (Y60) modified with tetraethylenepentamine (TEPA). They noticed that the surface characteristics of Y60 were significantly altered after TEPA grafting, leading to enhanced adsorption capacity toward CO₂, especially in the presence of water vapor.

2.1.3. Mesoporous silicon

Mesoporous silicon has a large specific surface area and a uniform pore size distribution in the range of 2–10 nm, which enable its broad application in the fields of adsorption, separation, and catalysis. Currently, the mesoporous silicon materials mainly used for CO₂ adsorption are M41S series [21] and SBA-x series [22]. The most common types of mesoporous silica are MCM-41 [23] and SBA-15 [24]. Unfortunately, pure silica surfaces do not provide strong adsorption sites for CO₂ because the residual hydroxyl groups are attached to the silica surface

after the template removal step. Thus, the mesoporous silicon fails to induce significant interactions with CO₂, and further specific adsorption sites are missing.

Surface modification is an interesting strategy to modify the surface properties and further increase the gas adsorption interaction. Harlick et al. [39,40] prepared a triethylamine-modified mesoporous silica molecular sieve TRI-PE-MCM-41, and the effects of amine grafting and water content on the CO₂ adsorption were investigated. The results showed that the adsorption capacity and rate of TRI-PE-MCM-41 were determined by the amount of amine grafting and water content. The adsorption capacity of TRI-PE-MCM-41 for CO₂ reached 2.65 mmol/g at 25 °C and 0.1 MPa. Table 2 summarizes the results of studies on the amino-functionalized ordered mesoporous silicates for CO₂ adsorption and separation. The enhancement in CO₂ adsorption by amine functionalization relies on the acid–base chemical interaction between CO₂ and amine groups [41], leading to the formation of carbamate or bicarbonate species. Under dry conditions, the reaction between CO₂ molecules and amine groups leads to the formation of carbamates. As another peculiarity, the presence of water vapor usually decreases their adsorption capacity; therefore, further development of amino-functionalized mesoporous silicates with water resistance is expected in the future.

2.2. Metal organic frameworks

MOFs known as coordination polymers are a relatively new class of porous materials with high diversity for application in gas separation, storage, and catalysis [25,26]. With a high specific surface area, the large amount of space inside and outside the channels makes the CO₂ adsorption capacity of MOFs far greater than that of the IPMs described earlier [52]. In 2005, Yaghi et al. [53] reported the adsorption capacity of CO₂ for a series of MOFs. MOF-177 had a volume capacity of 320 cm³ (STP)/cm³ and a mass capacity of 33.5 mmol/g at 25 °C and 35 bar, which are 2.17 and 4.53 times that for the commercial molecular sieve 13X and 1.97 and 1.34 times that for the activated carbon Maxsorb. In 2008, the volume capacity and mass capac-

ity of MIL-101 (Cr) prepared by Llewellyn et al. [54] were 390 cm³ (STP)/cm³ and 40 mmol/g at 31 °C and 50 bar, which was a new record for CO₂ adsorption capacity for MOFs. In 2010, Yaghi et al. [55] prepared MOF-210 with ultra-high porosity, and the record value increased to 54.5 mmol/g.

The current adsorption and separation technology is generally performed under moderate conditions; therefore, the CO₂ adsorption of MOFs at room temperature and atmospheric pressure is of practical significance [27,28]. Table 3 lists the CO₂ adsorption capacities of several types of MOF materials at room temperature and 1 bar, which reveals that the adsorption capacity of CO₂ is closely related to factors such as the content of unsaturated metal and –NH₂, which can interact strongly with CO₂ gas. Yaghi et al. [56] reported that the CO₂ adsorption capacity of Mg-MOF-74 with rich unsaturated Mg atoms reached as high as 8.48 mol/kg at 1 bar. Therefore, Mg-MOF-74 was regarded as an ideal CO₂ trapping material.

Amino modification has commonly been used as an effective way to improve the CO₂ selectivity of adsorbent materials. An et al. [64] prepared Bio-Mg-11 by grafting organic amines on Co-based MOFs. At 0 °C and atmospheric pressure, the saturated adsorption capacity of CO₂ was 6.0 mmol/g and the selectivity of CO₂/N₂ reached 75%. Couck et al. [65] modified MIL-53 (Al) with organic amines to increase its CO₂ adsorption capacity to 6.7 mmol/g with high selectivity of CO₂/CH₄.

In addition, MOFs are very sensitive to water vapor and impurities. To overcome these problems, researchers have improved their water resistance through modification [66–68]. For example, Cohen et al. [68] grafted long-chain alkyl groups onto IRMOF-3 to induce hydrophobicity. Li et al. [69] prepared anti-water vapor microporous amine-modified MOFs. At 25 °C and 1 bar, the adsorption capacity of CO₂ was 2.45 mmol/g, whereas that of CH₄ was only 2.68 × 10^{–5} mmol/g. The large separation coefficient (approximately 9.1 × 10⁴) in this work represented an important step in the synthesis of MOFs.

2.3. Microporous organic polymers

Compared with MOFs and inorganic porous materials, porous organic polymers can regulate gas adsorption performance over a wide range through modification of the functional groups and chain lengths of the building molecules. Because most microporous organic polymers (MOPs) exhibit good chemical and thermal stability, they have potential applications

Table 2

Amino-functionalized ordered mesoporous silicates for CO₂ adsorption.

Mesophase	Functionalizing agent	CO ₂ adsorption capacity (mol/kg)	Ref.
MCM-41	<i>N</i> -β-(aminoethyl)-γ-aminopropyl dimethoxy methylsilane	2.20	[42]
	Tetraethylenepentamine	5.39	[43]
	(3-Aminopropyl)trimethoxysilane	3.27	[44]
	Polyethylenimine	5.59	[45]
SBA-15	Tetraethylenepentamine	3.93	[46]
	Tetraethylene-pentamine/diethanolamine	3.70	[47]
	Aziridine-derived aminopolymers	5.55	[48]
	(3-Trimethoxysilylpropyl) diethylenetriamine	2.41	[49]
	Octa(3-aminophenyl) octasilsesquioxane	1.89	[50]
	Tris(2-aminoethyl)amine	1.59–1.82	[51]

Table 3

MOFs with higher CO₂ adsorption capacity under atmospheric pressure.

MOF	Surface area (m ² /g)		CO ₂ uptake (mol/kg)	<i>T</i> /°C	<i>P</i> /bar	Ref.
	BET	Langmuir				
MOF-74(Mg)	1495	1905	8.48	25	1	[57]
MOF-74(Co)	957	1388	7.55	25	1	[57]
MOF-74(Ni)	936	1356	7.15	25	1	[57]
bio-MOF-11	—	—	6.00	0	1	[58]
MOF-74(Zn)	816	—	5.54	23	1 atm	[59]
SIFSIX-2-Cu-i	735	821	5.41	25	1	[60]
CUK-1	310	—	3.48	25	760 torr	[61]
YO-MOF	—	335	3.39	0	1	[62]
SNU-M10	—	—	3.30	0	1	[63]

in gas storage, adsorption, separation, and heterogeneous catalysis.

For example, some covalent organic frameworks (COFs) can be repeatedly used and maintain their good CO₂ capture performance even under moist conditions [29]; therefore, COFs have been proposed as an excellent candidate for CO₂ capture. Since the first report on CO₂ adsorption of COFs in 2009, great efforts have been made to improve their CO₂ capture performance. A plot of low-pressure CO₂ uptake versus pore diameters for the selected COFs at 0 °C and 1 bar is presented in Fig. 3, showing that low-pressure CO₂ capture capacity is closely associated with the pore width of COFs. COFs with micropore diameters smaller than 1 nm usually possess large CO₂ uptake, and FCTF-1-600 with an ultra-micropore size of 0.46 nm exhibits the largest CO₂ capacity as high as 125 cm³/g. Thus, the construction of COFs with uniform micropores or ultra-micropores is favorable for the enhancement of the low-pressure CO₂ uptake. COFs with polar groups on the pore wall display much higher CO₂ capture capacity than those without polar groups, which can be attributed to the stronger interaction of the polar groups with CO₂ molecules [30]. Another criterion to evaluate the performance of porous materials is CO₂ capture in humid mixture gas. A breakthrough experiment was performed on FCTF-1 in a humid CO₂/N₂ (10:90) gas mixture at 25 °C and 1 bar [70]. The FCTF-1 saturated by water vapor only displayed a 12% decrease in CO₂ uptake and a small reduction in CO₂/N₂ selectivity (from 77% to 66%) compared with those in dry gas. Thus, the hydrophobic ultra-micropores of COFs help to maintain the CO₂ capture performance under humid conditions.

In addition to crystalline COFs, there are some MOPs with an amorphous organic skeleton. Compared with crystalline polymers, the preparation processes of amorphous MOPs are relatively facile and can be easily scaled up. Because of the cross-linked channels, amorphous MOPs possess ultra-high specific surface areas and therefore have large-scale application prospects. Many research groups [71–74] have made contributions to the field of amorphous porous polymers. Zhu et al. [75] prepared a porous polymer PAF-1 by substituting a C–C

Fig. 3. Plot of low-pressure CO₂ uptake against pore diameter for the selected COFs at 0 °C and 1 bar. Copyright permission from John Wiley and Sons, Ref. [30].

bond in the diamond structure with one (P1), two (P2), or three phenyl (P3) (Fig. 4). The specific surface area of these polymers was as high as 5600 m²/g, and the CO₂ adsorption reached 1300 mg/g at 25 °C and 40 bar. This result was a milestone in the preparation of MOP materials and gas storage. Subsequently, Zhou et al. [73] adopted the same strategy to prepare a porous polymer PPN-4 with a specific surface area of 6461 m²/g and a CO₂ adsorption capacity of 2121 mg/g at 22 °C and 50 bar.

Such polymers with ultra-high specific surface area have excellent high-pressure adsorption properties but low selectivity for low-pressure adsorption. The enhanced interaction between CO₂ molecules and the polymer framework increased the low-pressure adsorption capacity and selectivity. For example, Zhou et al. [74] grafted sulfonic acid groups and lithium sulfide onto the surface of these porous polymers. The CO₂ adsorption capacity of sulfonated grafted PPN-6-SO₃Li at 22 °C was 3.7 mmol/g with selectivity of CO₂/N₂ as high as 155/1, which was much higher than that of pristine PPN-6 (1.2 mmol/g).

2.4. Other applications

In addition to the special application in gas adsorption, the porous materials also showed potential for application in other fields. For example, the adsorption capacity and release of drugs could be easily controlled by adjusting the pore size and surface property of the porous materials. These porous materials can be used in biological fields as drug carriers for achieving drug release and improving the activity of drugs [76–78]. The porous carbons or MOFs/MOPs-derived carbons possessed high surface area, multi-dimensional channel structures, and electrical conductivity, which are favorable for rapid charge and mass transfer. These porous materials emerged as excellent electrode materials, supercapacitors, and anode materials

Fig. 4. (a) structure of diamond; (b) Structure model of P1; (c) Structure model of P2; (d) Structure model of P3. Copyright permission from John Wiley and Sons, Ref. [75].

for lithium-ion batteries [79–84]. Moreover, some of the porous materials enabled rapid adsorption of different targets, which can be regulated by the pore size. They showed potential for application in gas or liquid separation and pollutant elimination in environmental science fields [85–87].

3. Porous-material-based photocatalysts for CO₂ conversion

Although the CO₂ adsorption capacity has been improved by the modification of porous materials, the adsorption and separation technology cannot achieve the recycling of CO₂ resources. CO₂ recycling should include both adsorption and conversion. Adsorption is the basis of transformation, whereas the conversion of the adsorbed CO₂ can essentially alleviate the energy and environment problems from CO₂ emissions. Photocatalytic conversion of CO₂ is considered one of the most economical conversion methods because it uses solar energy to trigger the CO₂ reduction reaction (CRR) to produce chemical fuels (Fig. 5). As illustrated in Fig. 5(a), under light irradiation, the photogenerated electrons in the conduction band (CB) of semiconductors reduce CO₂ through a sequence of reactions. The final oxidation state of the carbon atom in the products is determined by the number and rate of electrons transferred [88]. First-principles calculations on the thermodynamically feasible formaldehyde pathways was performed (Fig. 5(b)) [89]. There are two reaction paths: path I, CO₂→HCOOH→H₂CO→CH₃OH→CH₄, and path II, CO₂→CO→H₂CO→CH₃OH→CH₄. The rate-determining step of path I is photoreduction of HCOOH to H₂CO, whereas that of path II is photoreduction of CO₂ to CO. The photoreduction of HCOOH to H₂CO has a kinetic barrier of 1.81 eV, which is much larger than that for the photoreduction of CO₂ to CO (1.41 eV). It would be more efficient if CO instead of formic acid is the precursor of formaldehyde. It was concluded that the conversion efficiency depends on two processes, the CO₂ adsorption and the effective electron transfer on the reaction sites of the photocatalysts. Currently, research on photocatalytic CRR has attracted widespread attention; however, the performance of many traditional semiconductor photocatalysts is not efficient enough to satisfy the re-

quirements for their practical applications because of their limited specific surface area and low CO₂ adsorption capacity. Upon introducing porous materials with high CO₂ uptake into the photocatalytic system, the CO₂ molecules can be adsorbed and enriched on the surface of the photocatalyst, presumably leading to remarkable enhancement of the CRR efficiency. Therefore, the construction of photocatalysts on porous materials is of great interest in the development of high-performance photocatalysts toward CRR application.

3.1. IPM-based photocatalysts

3.1.1. Porous carbon-based photocatalysts

The combination of porous carbon materials and photocatalysts will improve the catalytic CRR activity through the enlarged CO₂ adsorption capacity and photothermal synergistic effect. Wang et al. [90] reported the synthesis of hybrid carbon@TiO₂ hollow spheres using a carbon nanosphere template (Fig. 6). The optimized carbon@TiO₂ composites exhibited enhanced photocatalytic activity for CRR compared with commercial TiO₂ (P25). The photocatalytic CH₄ production rate (4.2 μmol g⁻¹ h⁻¹) was two times that of TiO₂. Moreover, a large amount of CH₃OH was produced (9.1 μmol g⁻¹ h⁻¹). The significantly improved photocatalytic activity resulted from the increased specific surface area (110 m²/g) and CO₂ uptake (0.64 mmol/g), together with the enhancement in light absorption and local photothermal effect by the carbon materials around the photocatalysts.

The proton reduction into H₂ is the main competitive process of CO₂ reduction, especially when using water as a reductant [91–95]. The H₂ evolution consumed the amount of photogenerated electrons for CRR [91,95]. To improve the selectivity of photocatalytic CRR in the presence of water, wrapping a carbon layer outside the photocatalyst causes more protons from the water splitting to participate in the CO₂ reduction, thereby facilitating the photocatalytic reduction of CO₂ to CO and CH₄. Pan et al. [96] reported that the use of In₂O₃ nanobelts coated with a 5-nm-thick carbon layer (C-In₂O₃) resulted in enhanced photocatalytic reduction of CO₂ with CO and CH₄ evolution rates of 126.6 and 27.9 μmol/h, respectively. The CO₂

Fig. 5. (a) Schematic energy diagram for water reduction/oxidation and CO₂ reduction (Copyright permission from Elsevier, Ref. [88]); (b) Full potential energy surfaces for the photoreduction of CO₂ to CH₄ (Copyright permission from American Chemical Society, Ref. [89]).

Fig. 6. (a) Illustration of the formation mechanism; (b) Photoexcitation process for the carbon@TiO₂ composite photocatalyst with hollow structure. Copyright permission from Royal Society of Chemistry, Ref. [90].

adsorption capacity on the C-In₂O₃-based catalyst reached a maximum value (2.2 mmol/g) that was larger than those on the pure In₂O₃ and pure carbon. The improved CO₂ chemisorption increased the probability of proton capture by the CO₂[−] and promoted the photocatalytic reduction of CO₂ to CO and CH₄.

In addition, it was proved that the CRR performance can be greatly enhanced by using carbon-based two-dimensional (2D) layered materials, namely graphitic carbon nitride (g-C₃N₄) and graphene because of their excellent electronic and physico-chemical properties [97]. Li et al. [98] prepared a g-C₃N₄-loaded Bi₂WO₆ photocatalyst, which exhibited 22 and 6.4 times higher CO production rates than pure g-C₃N₄ and Bi₂WO₆, respectively. Yu et al. [99] reported that the use of the graphene/CdS nanorod composite resulted in a photocatalytic production rate of CH₄ of 2.51 μmol h^{−1} g^{−1}, which was 10 times higher than that achieved on pure CdS. It is known that the 2D π-conjugated structure can participate in π–π interactions with CO₂ molecules, which also contain delocalized π-conjugated electrons. In this way, the CO₂ adsorption capacity can be improved, which led to the enhanced CRR performance.

3.1.2. Molecular-sieve-based photocatalysts

Molecular sieves such as zeolite can provide reaction sites within micropores, resulting in a high removal efficiency of volatile organic compounds [100]; hence, they enable certain selectivity for accessing reactants. The pore size effect is an important factor in determining the photocatalytic performance of molecular-sieve-based photocatalysts. Yuichii et al. [101] prepared Ti-MCM-41 and Ti-MCM-48 by loading TiO₂ onto porous zeolite via a hydrothermal method. In the reaction with CO₂ and H₂O under a 55 °C gas phase, Ti-MCM-48 exhibited higher catalytic activity and selectivity to CH₃OH because of its large pore size and three-dimensional channel structure. The introduction of molecular sieve supports has an important effect on the crystal structure of TiO₂; therefore, the selectivity of the product can be altered. Hiromi et al. [102] prepared ex-TiO₂/Y-zeolite, imp-TiO₂/Y-zeolite, and pure TiO₂ catalysts via the ion-exchange and impregnation methods. The ex-TiO₂/Y-zeolite catalyst showed higher selectivity to CH₃OH. The former TiO₂ had a tetrahedral structure, and the latter two

catalysts had octahedral structures. TiO₂ (Ti³⁺–O[−]) with a tetrahedral structure was inclined to the formation of CH₃OH.

The reactivity and selectivity of the zeolite catalyst can be also determined from the hydrophilic and hydrophobic properties of the zeolites. Ikeue et al. [103] prepared two types of catalysts using two different SDAs: Ti-Beta(OH) and Ti-Beta(F). Ti-Beta(OH) exhibited a higher reactivity than Ti-Beta(F), and the selectivity for the formation of CH₃OH on Ti-Beta(F) was higher than that on Ti-Beta(OH). The hydrophilic Ti-Beta zeolite (Ti-Beta(OH)) exhibited a more dramatic increase in the coordination number than the hydrophobic Ti-Beta(F) zeolite. These results suggest that CO₂ and H₂O molecules can be adsorbed efficiently onto the highly dispersed tetrahedrally coordinated titanium oxide species.

3.1.3. Mesoporous-silicon-based photocatalysts

Heterogeneous photocatalysis has a high efficiency for the removal of highly toxic and non-biodegradable pollutants [104–106]. TiO₂ supported on SiO₂ and derivatives such as SiO₂ films [107], MCM-41, and MCM-48 and SBA-15 [108,109] have been reported to exhibit high photocatalytic activity. Lin et al. [110] prepared DCQ-TiO₂/SBA-15, and the photocatalytic reduction of CO₂ in water was conducted under visible-light illumination. The methanol yield over DCQ-TiO₂/SBA-15 was 0.44 μmol g_{cat}^{−1} h^{−1}, which was much higher than that of DCQ-P25 TiO₂ (0.16 μmol g_{cat}^{−1} h^{−1}). The higher photocatalytic activity of DCQ-TiO₂/SBA-15 was attributed to the larger amounts of adsorbed DCQ by the ordered nanochannels. Similarly, mesoporous-SiO₂-supported catalysts are also suitable for gas–solid phase reactions. Li et al. [111] used a one-pot sol–gel method for the synthesis of Cu/TiO₂-SiO₂ catalysts, and the photocatalysis was performed at a gas–solid interface. Pristine TiO₂ had the lowest production rate, 8.1 μmol g_{TiO2}^{−1} h^{−1} for CO. With the introduction of the mesoporous SiO₂ support, the CO production increased to 22.7 μmol g_{TiO2}^{−1} h^{−1}. This improvement may be due to the improved dispersion of TiO₂ nanoparticles and enhanced adsorption of CO₂ and H₂O on the high surface area of the SiO₂ substrate. Coupling mesoporous SiO₂ with layered semiconductor materials exposed more active sites at the interface between SiO₂ and the semiconductor, which is favorable for photocatalytic CRR. Li et al. [112] prepared lamellar HNb₃O₈ pillared with silica for CO₂ photoreduction by H₂O under ultraviolet (UV) light irradiation (Fig. 7). The yield of methane reached 2.9 μmol g_{cat}^{−1} h^{−1} over SiO₂-HNb₃O₈, which is six times that over non-pillared HNb₃O₈ (0.47 μmol g_{cat}^{−1} h^{−1}). The SiO₂ pillared HNb₃O₈ sample had a notably expanded interlayer distance and much greater surface area than the nonpillared HNb₃O₈. Thus, the reaction active sites at the interlayer space of SiO₂-HNb₃O₈ should have been more accessible to the substrates. In addition, the SiO₂-HNb₃O₈ sample exhibited unique intercalation behavior for water molecules through hydrogen bonding, which also contributed to the enhanced activity.

3.2. MOF-based photocatalysts

MOFs, a novel class of porous materials consisting of metal-containing clusters and organic ligands, have attracted

Fig. 7. (A) TEM and (B) SEM images of SiO₂-pillared HNb₃O₈; (C) Photocatalytic reduction of CO₂ over (a) SiO₂-HNb₃O₈, (b) HNb₃O₈, and (c) Nb₂O₅. Copyright permission from American Chemistry Society, Ref. [112].

growing interests in diverse fields, particularly in gas adsorption/separation and catalysis. In addition to their high gas uptake capability, MOFs are semiconductors or insulators with a band gap of 1.0–5.5 eV. Under light irradiation, the ligands can capture photons, resulting in electron transfer from the ligands to the metal. To improve the photocatalytic activity of MOFs, two crucial problems need to be addressed: broadening the spectral response range and improving the quantum efficiency.

The modification of MOF materials by chromophores, chelates, or metal complexes is an effective way to extend the spectral response range. For example, Sun et al. [113] reported MOF-253-Ru(CO)₂Cl₂ for photocatalytic CRR (Fig. 8). The pure MOF-253 alone did not show absorption in the visible-light region. When coordinating to Ru(II) via N,N-chelating sites, the absorption edge of the as-prepared MOF-253-Ru(CO)₂Cl₂ extended to 470 nm. Approximately 0.67 μmol of HCOO[−], 1.86 μmol of CO, and 0.09 μmol H₂ were produced after irradiation for 8 h. Another report introduced ruthenium-based dye as a photosensitizer to cooperate with ZIF-67 material. The photocatalytic performance toward CRR increased to 37.4 μmol/30 min for the CO generation rate [114].

Recent studies [115–117] have reported that some MOF materials such as UiO-66 can exhibit semiconductor behavior with active sites for the photocatalytic CRR despite their rather low efficiency. To improve the quantum efficiency, the re-

searchers explored various MOF materials with high CO₂ capture capacity for coupling with photocatalysts. Yan et al. [118] fabricated a Co-ZIF-9/TiO₂ composite (ZIFx/T) with a well-designed nanostructure in which TiO₂ and Co-ZIF-9 were closely bound with each other. After 10 h of UV-visible light irradiation, ZIF0.03/T exhibited the highest photocatalytic activity with a total N_{UPN} (UPN, utilized photoelectron number) of 28.17 μmol, which was approximately 2.1 times that of the pure TiO₂. The well-ordered porous structure and imidazolate motifs of Co-ZIF-9 are essential for CO₂ adsorption/activation and thus result in the superior CRR activity. This work revealed that coupling TiO₂ with MOFs greatly improved the photocatalytic activity toward CRR as compared with pure TiO₂. To achieve further utilization of the visible region in solar energy, MOF materials could be combined with semiconductors that are responsive to visible light. A series of Cd_{0.2}Zn_{0.8}S@UiO-66-NH₂ nanocomposites with different UiO-66-NH₂ contents were fabricated via a solvothermal method [119]. The optimal composite (20 wt% of UiO-66-NH₂) exhibited a CH₃OH production rate of 6.8 μmol h^{−1} g^{−1} under visible-light irradiation. This remarkable enhancement of the photocatalytic activity can be attributed to the efficient charge separation and transfer on the interface between Cd_{0.2}Zn_{0.8}S and UiO-66-NH₂. Liu et al. [120] decorated tubular g-C₃N₄ with transparent zeolitic imidazolate framework-8 (ZIF-8) nanoclusters. The photocatalytic rate of

Fig. 8. (a) Amount of products produced as a function of irradiation time over MOF-253-Ru(CO)₂Cl₂; (b) Proposed mechanism for photocatalytic CRR over the as-prepared MOF-253-Ru(CO)₂Cl₂ under visible light. Copyright permission from Royal Society of Chemistry, Ref. [113].

CH₃OH production reached 0.75 $\mu\text{mol h}^{-1} \text{g}^{-1}$, which was more than 3 times greater than that of bulk g-C₃N₄ photocatalysts. Nanosized carbon nitride nanosheets were incorporated with UiO-66 for photocatalytic CRR (Fig. 9). This hybrid structure exhibited a large surface area and strong CO₂ capture ability due to the introduction of UiO-66. The UiO-66/CNNS composite exhibited a high CO yield of 59.4 $\mu\text{mol/g}_{\text{CN}}$ under visible-light illumination for 6 h; this value was more than three times that of CNNS (17.1 $\mu\text{mol/g}_{\text{CN}}$) [121].

In addition to MOFs cooperating with semiconductors, there are several reports about combining MOF materials with metal nanoparticles. As reported by Choi et al. [122], Ag nanocubes with surface plasma resonance (SPR) effect were coated with Re-MOF to form Ag@Re₃-MOF (Fig. 10). The SPR-based photocatalysts exhibited 5-fold enhancement of activity over Re₃-MOF under visible light. Moreover, the ReTCs covalently binding within the MOFs benefited their long-term stability. Zhang et al. [123] discovered that anchoring atomically dispersed catalysts (e.g., mononuclear metal complexes or single metal atoms) on supports resulted in maximum atom efficiency. They coordinatively incorporated an unsaturated single atom into a MOF matrix. The porphyrin MOFs comprising atomically dispersed catalytic centers exhibited significantly enhanced photocatalytic conversion of CO₂, which was equivalent to a 3.13-fold improvement in the CO evolution rate (200.6 $\mu\text{mol g}^{-1} \text{h}^{-1}$) and a 5.93-fold enhancement in the CH₄ generation rate (36.67 $\mu\text{mol g}^{-1} \text{h}^{-1}$) compared with those of the parent MOFs. The results revealed that the presence of single Co atoms in the MOF can greatly boost the electron-hole separation efficiency in porphyrin units.

3.3. MOP-based photocatalysts

Compared with other porous materials, MOP materials possess remarkable stability in strong acidic and basic mediums [124]. Most MOP-based catalysts can be divided into two types.

Fig. 10. (a) TEM image of Ag@Re₃-MOF catalyst; (b) Scheme of CO₂ photoreduction over Ag@Re₃-MOF catalyst. Copyright permission from American Chemistry Society, Ref. [122].

In one type, the nonmetallic catalytic active center is embedded into the skeleton to construct intrinsic polymer catalysts, and in the other type, catalyst particles or ions are loaded on the surface or within the channels of MOP supports. As typical MOP materials, COFs with a large π -conjugated structure possess excellent CO₂ absorption capacity and conductivity. In addition, their high surface area and tunable porosity as well as crystalline and stable skeletons make them attractive support matrices for loading nanoparticles [125]. Thus, COFs with visible light absorption show potential for application in the field of photocatalysis [126].

In 2013, Schwinghammer et al. [127] prepared triazine-doped metal salts PTI/Li⁺Cl⁻ and heptazine-based COFs, which displayed photocatalytic activity with hydrogen production rates of 864 and 722 $\mu\text{mol h}^{-1} \text{g}^{-1}$, respectively. In 2014, Lotsch et al. [128] prepared hydrazone-linked nitrogen-rich TFPT-COF materials with visible-light-driven photoactivity (Fig. 11). The hydrogen production efficiency reached as high as 1970 $\mu\text{mol h}^{-1} \text{g}^{-1}$, and the quantum efficiency reached 2.2% in the presence of 10% triethanolamine solution as an electron sacrificial agent. Thote et al. [129] deposited CdS nanoparticles on a two-dimensional (2D) COF matrix. The CdS-COF (90:10) hybrid exhibited a hydrogen production rate of 3678 $\mu\text{mol h}^{-1} \text{g}^{-1}$, which was significantly higher than that of bulk CdS parti-

Fig. 9. (a) Schematic illustration of the preparation of the UiO-66/CNNS heterogeneous photocatalyst; (b) Time course of CO evolution over bulk CN, CNNS, UiO-66/bulk CN, and UiO-66/CNNS photocatalysts; (c) Proposed mechanism of photocatalytic reduction of CO₂ by the UiO-66/CNNS heterogeneous photocatalyst under visible-light irradiation. Copyright permission from John Wiley and Sons, Ref. [121].

Fig. 11. Design and synthesis of TFPT-COF. Copyright permission from Royal Society of Chemistry, Ref. [128].

cles ($124 \mu\text{mol h}^{-1} \text{g}^{-1}$). The structural merits of the COF materials, such as the π -conjugated structure, high surface area, and abundant 2D hetero-interface, highlighted their effectiveness as supports for stabilizing the catalyst nanoparticles and improving the charge carrier separation, thereby resulting in a high photocatalytic activity.

Research on MOP-based photocatalysts has mainly focused on photocatalytic hydrogen production. To date, there are no reports on photocatalytic CO_2 conversion to the best of our knowledge. The absence of MOPs in photocatalytic CRR can presumably be attributed to their low photocatalytic performance relative to semiconductor photocatalysts according to recent reports. For example, biphenyl and bipyridine copolymers containing trace amounts of Pt exhibited apparent quantum efficiency (AQE) of hydrogen production of only 1.8% at 350 nm [130]. In addition, the AQE of conjugated microporous polymer by benzene-ring crosslinking was only 2.3% toward hydrogen production at 420 nm [131]. Although there are extensive reports on their use for gas adsorption/separation and catalysis, the application of MOP-based photocatalysts toward CRR is worthy of in-depth study in the future.

3.4. Other modifications of photocatalysts

In addition to combining photocatalysts with porous materials, there are other modifications that can be used to enhance the adsorption and photocatalytic reduction performance of CO_2 , such as alkali modification, impurity doping, metal deposition, and heterojunction construction [132–134]. The alkali modification of photocatalysts has been considered one of the most efficient ways to enhance the adsorption capacity of CO_2 by enabling chemisorption through alkali sorbents and then improving the photocatalytic CO_2 reduction efficiency. For example, Meng et al. [135] demonstrated that the alkali modification of TiO_2 by NaOH could greatly improve the chemisorption and activation of CO_2 on TiO_2 photocatalysts. The photocatalytic CO_2 reduction activity of the optimal sample calcined with 3 wt% of NaOH was observed to be far higher than that of pure

TiO_2 . The introduction of NaOH can activate the CO_2 molecule by promoting the formation of bidentate carbonate species. Liu et al. [136] reported an earth-abundant alkaline mineral, MgO coupled TiO_2 (MgO-TiO_2), for enhancing the photocatalytic CO_2 reduction activity. The addition of MgO significantly enhanced the CO_2 adsorption ability of TiO_2 and limited the adsorption of H_2O molecules. Therefore, the competitive H_2O water splitting reaction on conventional photocatalysts could be avoided on the MgO-TiO_2 .

Table 4 summarizes the findings of recent reports on CO_2 reduction in both gas-liquid and gas-solid reaction systems. The production rates of the main products, such as CO, CH_4 , and CH_3OH over these photocatalysts were very low. After alkali modification on photocatalysts, because of the chemical adsorption with CO_2 molecules in the photocatalytic process, the CRR catalytic efficiency increased to approximately 2 times that of the pristine photocatalysts. In particular, when combining the porous materials with semiconductors, the conversion efficiency of CO_2 molecules appeared to significantly improve, and the change was more notable than with the other modifications. This improvement could be attributed to the improved CO_2 adsorption by porous materials with larger surface area, especially in the MOF-based photocatalytic system.

Even though a great enhancement in activity has been achieved, the current state of photocatalytic CO_2 reduction is far from satisfactory for practical applications. Many open issues and challenges remain, which require further research efforts. First, these porous materials suffer from a certain degree of instability in the processes of CO_2 adsorption and photocatalytic reduction, such as the poor water resistance of IPMs, thermal-/photo-instability of MOFs and MOPs, and poor stability under acidic or alkaline conditions. Second, the specific surface area and CO_2 adsorption capacity substantially decreased after incorporating photocatalysts into the porous materials. Finally, the mechanism of photocatalytic CO_2 reduction is not yet clear, which has restricted the development of efficient photocatalysts. Therefore, more studies in this field are urgently needed to explore new synthesis methodologies and in-depth mechanisms for further enhancing the photocatalytic performance of porous materials toward CO_2 conversion.

4. Conclusions and perspectives

In summary, this review highlighted the significant achievements made in the design and fabrication of porous nanomaterials for adsorption and photocatalytic conversion of the “greenhouse gas” CO_2 . According to the systematic research on gas adsorption and separation, the construction of photocatalysts toward CO_2 conversion is based on three classes of porous nanomaterials: IPMs, MOFs, and MOPs. Compared with IPMs, MOFs and MOPs possess distinct superiority in supporting photocatalysts for CRR because of their high surface area, tunable pore structures, and feasible skeleton modification. Benefiting from the improved CO_2 uptake capacity, the porous-material-based photocatalysts have exhibited remarkably enhanced efficiency in the reduction of CO_2 to chemical fuels, such as CO, CH_4 , and CH_3OH . The results are compared and

Table 4Summary of recent reports on CO₂ conversion efficiency over porous-material-based photocatalysts.

Catalyst	Light source	co-catalyst	Products (μmol g ⁻¹ h ⁻¹)	Ref.
<i>I. Gas-liquid reaction system</i>				
<i>i. Traditional photocatalyst</i>				
g-C ₃ N ₄	300 W Xe lamp	Pd	CH ₄ : 0.4 CH ₃ OH: 3.17	[137]
N-TiO ₂ MS	300 W Xe lamp		CH ₃ OH: 0.36	[138]
<i>ii. Porous material-based photocatalyst</i>				
carbon@TiO ₂ hollow spheres	300 W Xe lamp	—	CH ₄ : 4.2 CH ₃ OH: 9.1	[90]
DCQ-TiO ₂ /SBA-15	100W halide lamp	—	CH ₃ OH: 0.44	[110]
Cd _{0.2} Zn _{0.8} S@UiO-66-NH ₂	Visible light irradiation (λ > 420 nm)	—	CH ₃ OH: 6.8	[119]
g-C ₃ N ₄ /ZIF-8	300 W Xe lamp	—	CH ₃ OH: 0.75	[120]
MOF-253-Ru(CO) ₂ Cl ₂	Visible light irradiation (λ > 420 nm)	—	HCOO ⁻ : 16.75 CO: 46.5	[113]
<i>II. Gas-solid reaction system</i>				
<i>i. Traditional photocatalyst</i>				
S-TiO ₂	Visible light irradiation (λ > 400 nm)		CH ₄ : 3.3	[139]
TiO ₂ /g-C ₃ N ₄	Visible light irradiation (λ > 400 nm)	—	CO: 0.84 CH ₄ : 5.21	[140]
NaOH-TiO ₂	300 W Xe lamp		CH ₄ : 8.7	[135]
MgO-TiO ₂	400 W Xe lamp		CO: 21.0	[136]
<i>ii. Porous material-based photocatalyst</i>				
C-In ₂ O ₃	300 W Xe lamp	2 wt% Pt	CO: 126.6 μmol/h CH ₄ : 27.9 μmol/h	[96]
Cu/TiO ₂ -SiO ₂	Xe arc Lamp	0.5 wt% Cu	CO: 60 CH ₄ : 10	[111]
SiO ₂ -HNb ₃ O ₈	350 W Xe lamp	0.4 wt% Pt	CH ₄ : 2.9	[112]
Co-ZIF-9/TiO ₂	300 W Xe lamp	—	CO: 0.879 μmol/h CH ₄ : 0.099 μmol/h	[118]
UiO-66/CNNS	Visible light irradiation (λ > 420 nm)	—	CO: 9.9 μmol g _{CN} ⁻¹ h ⁻¹	[121]
ZIF-67 co-operated with [Ru(bpy) ₃]Cl ₂ ·6H ₂ O	Visible light irradiation (λ > 420 nm)	ZIF-67	CO: 37.4 μmol/30 min	[114]
MOF-525-Co	Visible light irradiation (λ > 420 nm)		CO: 200.6 CH ₄ : 36.76	[123]

summarized in Table 4. It is noteworthy that the CO₂ adsorption and conversion efficiency remain far from those needed for practical application in carbon resources recycling. Many open issues and challenges remain, which require further research efforts. First, more studies are needed to improve the stability of porous materials, such as the water resistance of IPMs and thermal/photo-stability of MOFs and MOPs. Second, the development of high-performance photocatalysts on porous supports without sacrificing the CO₂ adsorption capacity is highly desired. Finally, the in-depth study of the photocatalytic mechanisms of CRR must be reinforced to provide theoretical foundations to boost further advancements in this field. Overall, we believe that the development of porous photocatalysts with high CO₂ uptake is a direction with high potential that is worthy of further investigations for photocatalytic CO₂ conversion.

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Graphical Abstract

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Review on porous nanomaterials for adsorption and photocatalytic conversion of CO₂

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This review summarizes advances in the development of porous materials for CO₂ adsorption and photocatalytic conversion. Benefiting from improved CO₂ uptake, porous photocatalysts exhibit remarkably enhanced efficiency in the reduction of CO₂ to chemical fuels.

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多孔材料的二氧化碳吸附与光催化转化研究进展

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摘要: 太阳能光催化是CO₂转化和利用的新兴技术, 直接利用洁净充足的太阳能将自然界富有的“温室气体”CO₂转化成化学燃料, 不仅有利于消除大气温室效应, 而且能缓解能源短缺问题, 因而成为人们研究的一个重要方向。但目前CO₂的吸附和转换效率还很低, 这是太阳能光催化CO₂资源化的最大障碍。高性能光催化剂和合成是这项技术的关键。针对CO₂光还原反应的特异性, 理想的光催化材料应该具有以下功能: 强的CO₂吸附能力和高的光催化活性。将光催化剂与对CO₂具有高吸附性的多孔材料结合, 就可以将CO₂吸附并富集在吸附剂周围的光催化剂表面上以进行催化转化, 因此基于高效多孔吸附材料构筑光催化体系成为光催化转化CO₂的重要研究方向之一。

CO₂的循环利用包括吸附和转化两方面, 高吸附量的多孔材料是获得CO₂高转化效率的前提。本文首先以多孔材料结构参数及性能指标为主线, 对无机多孔材料、金属有机框架材料及微孔有机聚合物材料的研究进展及应用前景进行了评述。通过对多孔材料的改性和新型多孔材料的开发, CO₂的吸附能力得到一定的提升, 但是仅仅依靠多孔材料的吸附分离, 不能实现CO₂中的碳资源循环。在此基础上, 本文重点评述了多孔光催化材料在CO₂光催化转化中的最新研究进展。采用多孔材料与光催化剂结合, 可增加材料的比表面积, 在界面处暴露更多的活性位点, 有利于光催化CO₂转化的进行; 同时, 通过孔结构和基团调控, 可以调控光催化剂的反应活性和产物选择性。特别是金属有机框架材料与微孔有机聚合物材料, 改变构建单元的官能团和制备技术还可以实现光谱响应范围的调控, 提高太阳光的利用率。大量文献对比发现, 引入较高CO₂吸附效率的多孔材料构建光催化体系, CO₂光催化转化的效率及产物选择性显著提高。

最后, 本文对多孔材料在CO₂光催化转化领域的研究现状与亟待解决的问题进行了剖析, 提出了下一步可能的研究方向: (1) 提高多孔材料自身的稳定性如耐水性能与光/热稳定性; (2) 发展光催化材料在多孔载体的微观组装方法, 不影响CO₂吸附效率的前提下提高光催化活性; (3) 深入研究多孔光催化材料内部与表面的CO₂转化机理, 为进一步提高吸附与转化效率提供理论指导。

关键词: 多孔材料; 纳米复合材料; 二氧化碳吸附; 光催化; 二氧化碳转化

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