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Published in:
Industrial and Engineering Chemistry Research

Link to article, DOI:
[10.1021/acs.iecr.5b03277](https://doi.org/10.1021/acs.iecr.5b03277)

Publication date:
2016

Document Version
Publisher's PDF, also known as Version of record

[Link back to DTU Orbit](#)

Citation (APA):
Yuan, Z., Eden, M. R., & Gani, R. (2016). Toward the Development and Deployment of Large-Scale Carbon Dioxide Capture and Conversion Processes. *Industrial and Engineering Chemistry Research*, 55(12), 3383-3419. <https://doi.org/10.1021/acs.iecr.5b03277>

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Toward the Development and Deployment of Large-Scale Carbon Dioxide Capture and Conversion Processes

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S Supporting Information

ABSTRACT: In light of the depletion of fossil fuels and the increased daily requirements for liquid fuels and chemicals, CO₂ should indeed be regarded as a valuable C₁ additional feedstock for sustainable manufacturing of liquid fuels and chemicals. Development and deployment of CO₂ capture and chemical conversion processes are among the grand challenges faced by today's scientists and engineers. Very few of the reported CO₂ capture and conversion technologies have been employed for industrial installations on a large scale, where high-efficiency, cost/energy-effectiveness, and environmental friendliness are three key factors. The CO₂ capture technologies from stationary sources and ambient air based on solvents, solid sorbents, and membranes are discussed first. Transforming CO₂ to liquid fuels and chemicals, which are presently produced from petroleum, through thermochemical, electrochemical, photochemical, and biochemical routes are discussed next. The relevant state-of-the-art computational methods and tools as a complement to experiments are also briefly discussed. Finally, after pointing out the advantages and disadvantages of the currently available technologies for CO₂ capture and conversion, ideas and perspectives for the development of new techniques, opportunities, and challenges are highlighted.

1. INTRODUCTION

Fossil fuels will remain the primary resource for liquid transportation fuels and bulk-chemicals along with electricity required by modern society in the foreseeable future. The associated massive global CO₂ emissions, however, have led to escalating concentrations of atmospheric CO₂ to around 400 ppm.¹ Energy-intensive fossil fuel combustion for electricity generation is the largest contributor of life-cycle CO₂ emissions.² To manage efficiently the CO₂ emissions and moderate the relevant adverse consequences in the near future, a portfolio of high-profile collaborative initiatives on CO₂ capture, sequestration, and conversion to formulate a CO₂ recycle value chain as the most promising approach for suppressing CO₂ emissions has been launched,³ as illustrated by Figure 1.

The enhanced oil recovery coupled with the permanent sequestration underground in depleted oil fields, gas fields, coal beds, or other suitable geological formations are two well-established and mature pathways to processing the captured CO₂. Stringent CO₂ monitoring, verification, and accounting efforts to ensure that the injected CO₂ remains in the underground geologic formation are required. In addition, potential leakage, earthquakes, global capacity, economics, engineering feasibility, and the scale of deployment associated with CO₂ capture make geologic sequestration a controversial option.^{4,5} Although CO₂ sequestration is an important component for a viable future CO₂ value chain, a detailed review on this topic is outside the scope of this paper.

Rather than a pollutant that needs to be sequestered, CO₂ could be viewed as an abundant and inexpensive C₁ feedstock for the production of liquid transportation fuels, chemicals, and

other chemical-related products. Around the world, a great number of researchers have strategically moved their focus from understanding physical/chemical properties of long-term geological storage toward the economical and sustainable chemical conversion of captured CO₂. The concept, development, and deployment of a green, high-efficiency, and cost-effective CO₂ capture and conversion technology can not only help the society make fossil fuel utilization cleaner, safer, and more sustainable but also offer the development of a more sustainable energy economy.⁶

Through a brief overview of existing CO₂ capture and conversion technologies from the experimental and computational perspectives (very few of which have seen large-scale industrial implementation), this review pays particular attention to identifying the drawbacks and barriers that prohibit their implementation. Opportunities, challenges, and potential solutions are then highlighted. Moreover, the importance of multidisciplinary collaborations, as shown in Figure 2, among material scientists, chemists, chemical engineers, process systems engineers, and environmental engineers is emphasized.

The paper is structured as follows: First, existing CO₂ capture technologies including conventional chemical absorption, solid sorbent driven adsorption, and membrane separation are discussed in section 2. Section 3 reviews the main CO₂ conversion

Special Issue: Sustainable Manufacturing

Received: September 3, 2015

Revised: November 24, 2015

Accepted: November 30, 2015

Published: November 30, 2015

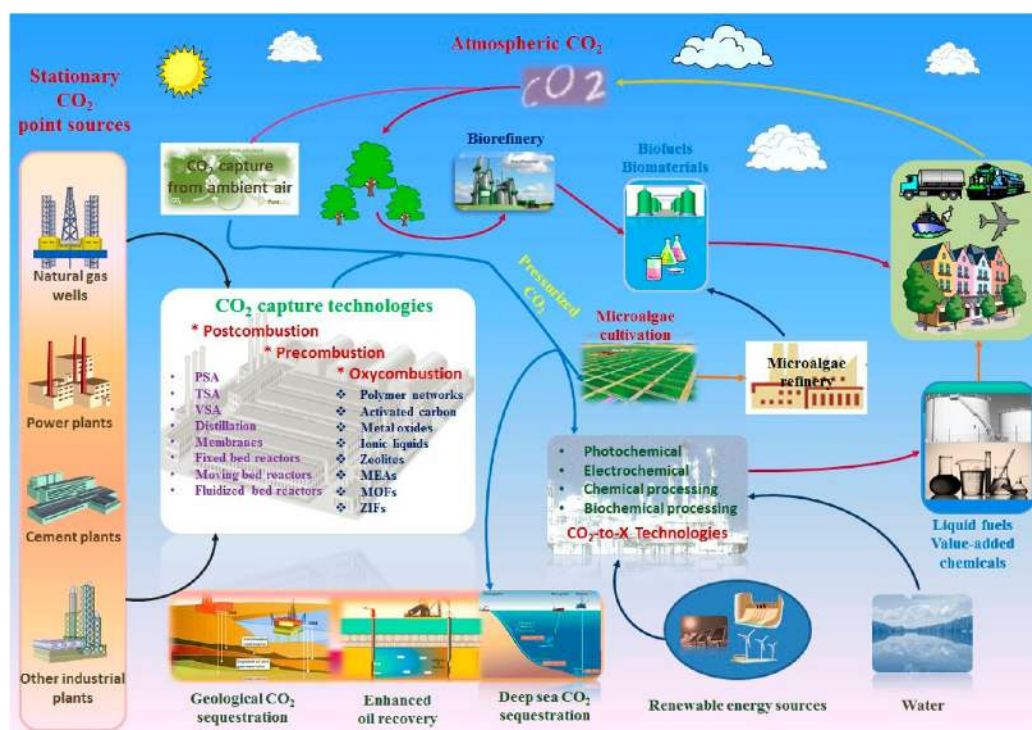


Figure 1. Value chain of carbon dioxide.

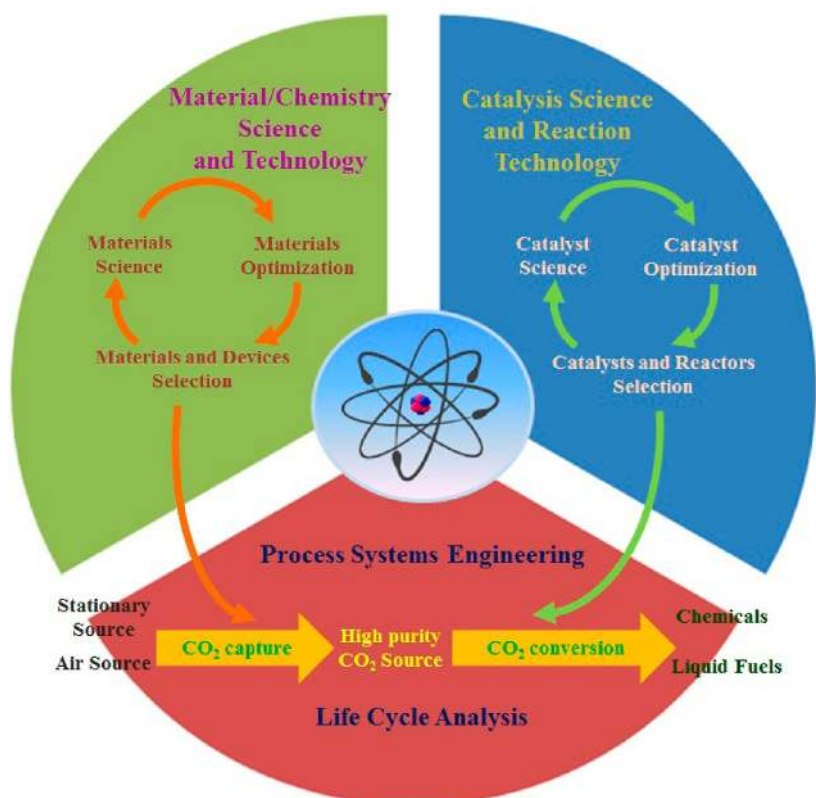


Figure 2. Schematic diagram of the integrated CO₂ capture and conversion scheme.

routes that comprise thermochemical, biochemical, photochemical, and electrochemical approaches. Section 4 focuses on computational tools and approaches for CO₂ value chain design including materials discovery, unit simulation and optimization, and supply chain management. Challenges and future research directions are then briefly discussed followed by the Conclusions.

2. CO₂ CAPTURE TECHNOLOGY

The aim of CO₂ capture is to remove selectively CO₂ from process streams and ambient air to produce a concentrated CO₂ stream that can be subsequently compressed and transported to nearby processing sites. As outlined in Figure 3, the main CO₂ resources are classified as stationary points (process streams) and

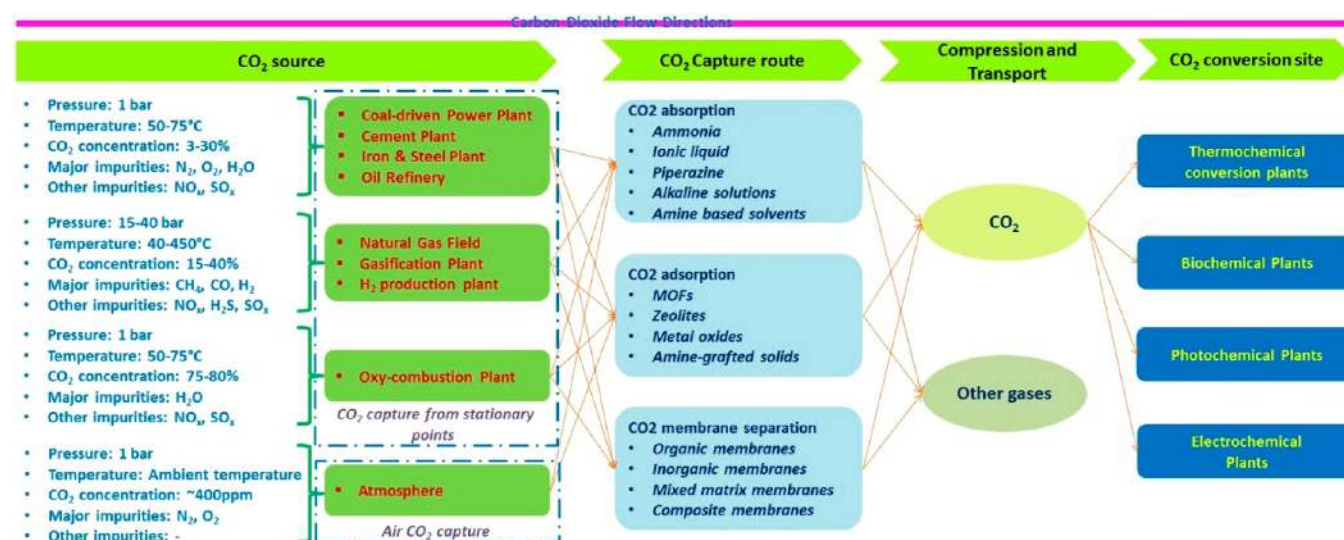


Figure 3. Summary of the main CO₂ sources and the existing capture technologies.

atmospheric (ambient air) and the three main capture routes are absorption, adsorption, and membrane-based separations. In this section, each CO₂ source and the corresponding capture technologies are reviewed.

2.1. Capturing CO₂ from Stationary Points. CO₂ capture from stationary point sources, such as coal power plants (mainly CO₂/N₂ mixtures), natural gas wells (mainly CO₂/CH₄ mixtures), and gasification plants (mainly CO₂/H₂ mixtures), is deemed a factor of paramount importance when dealing with CO₂ emissions. The capture technologies corresponding to each scenario with specific temperatures and CO₂ partial pressures require different capture materials. For example, to separate CO₂/H₂ from biomass/coal gasification plants, a solvent resistant to high temperature would remove the need for a cooling unit to lower the synthesis gas temperature. Consequently, numerous projects and initiatives have concentrated on the discovery of novel materials and innovative engineering solutions to bring down the total cost and to maximize the capture efficiency. Fine-tuning of the conditions to satisfy the thermodynamic and kinetic constraints related to the interaction between CO₂ and the capture material has been found to have a great potential for minimizing the energy requirements and thus improving the energy efficiency of CO₂ capture processes.⁷ Selectivity, affinity, and stability are three vital parameters for any material to be used for CO₂ capture.⁸ A wide range of capture materials, including liquid solvents, solid sorbents, and membranes, have been proposed for CO₂ capture. In the text below, their potential and obstacles for implementation are discussed.

2.1.1. Conventional Solvents. Physical absorption, which depends on temperature/pressure differences, and chemical absorption, which relies upon the acid-based neutralization reaction, are two major options for conventional solvent-based CO₂ capture. The main operations involving the solvent-based CO₂ capture are as follows:

- The gaseous stream containing CO₂ is contacted with the solvent and then absorbed in an absorber column at a relatively low temperature.
- The CO₂-rich solvent is pumped to a desorption column where it is regenerated by stripping with steam at elevated temperature to release the absorbed CO₂.

- The regenerated CO₂-lean solvent is subsequently returned to the absorber column.
- The absorber and the stripper are connected by heat exchangers.

Table 1 lists the main solvent-based technologies together with the advantages and disadvantages regarding their use.

Chemical Absorption. State-of-the-art chemical-absorption-based CO₂ capture technologies employ ammonia, aqueous amine/monoethanolamine (MEA) and alkali absorbents as solvents.⁹ Tertiary amines such as *N*-methyl-diethanolamine (MDEA) are commonly employed for natural gas sweetening, whereas aqueous amines, predominantly alkanolamine MEA, has been mainly employed for the removal of CO₂ from natural gas and hydrogen.¹⁰ The Fluor Econamine FG PlusSM (EFG+) technology, KM-CDR, and the Kerr-McGee/AGG Lummus Crest (KMALC) technology are three main amine-based commercial absorption routes for CO₂ capture. Historically, 30% MEA has served as the standard for the assessment of postcombustion CO₂ capture processes. In general, the CO₂ loading capacity for primary and secondary amines is in the range 0.5–1 mol of CO₂ per mol of amine. To some extent, higher amine concentrations containing less water results in smaller equipment size and thus reduces the capital cost. Enhanced strategies such as additional inhibitors and unusual materials for infrastructure construction may be able to overcome some of the known limitations of this type of technology. Mixed-amine-based solvents may offer superior capture performance such as low energy requirement in the stripping stage, fast reaction rate, and low chemical reactivity with flue gas impurities. The piperazine (PZ) is just one example of a mixed-amine-based solvent that can exhibit promising performance for postcombustion CO₂ capture.¹¹ Apart from various chemical amines, inorganic solvents such as aqueous ammonia can also be employed as a solvent for chemically absorbing CO₂ from flue gas and natural gas streams. This process relies upon a temperature swing to cycle between ammonium carbonate and ammonium bicarbonate.

Physical Absorption. Unlike the chemical solvents, the absorption capacity of physical solvents is proportional to the CO₂ partial pressure. In other words, they are suitable for precombustion CO₂ capture. To date, Selexol, Rectisol, Fluor,

Table 1. Main Solvent-based CO₂ Capture Technologies and Relevant Advantages/Disadvantages

type	existing commercial technology	solvent	optimal working condition	main application	advantage	disadvantage
chemical absorption		ammonia	14.5 psi CO ₂ ; 15–27 °C	CO ₂ /N ₂	high CO ₂ loading capacity	high volatility equipment plugging
chemical absorption	EFG Plus SM KM-CDR Kerr-McGee	amine base	14.5 psi CO ₂ ; 40–60 °C	CO ₂ /N ₂	effective at low pressure; mature technology	extensive energy penalty; sensitive to impurities
chemical absorption		piperazine	14.5 psi CO ₂ ; up to 150 °C	CO ₂ /N ₂	low degradation; effective at relative high temperature	low solubility; high production cost
physical absorption	Selexol	CH ₃ O(C ₂ H ₄ O) _n CH ₃	450 psi CO ₂ ; 0–5 °C	CO ₂ /H ₂	high solubility; no chemical reaction; noncorrosive	low efficiency at low pressures
physical absorption	Rectisol	chilled methanol	250 psi CO ₂ ; –30–+100 °C	CO ₂ /H ₂	high chemical stability; high thermal stability	form amalgams; expensive refrigeration; high capital cost
physical absorption	Fluor	propylene carbonate	250–850 psi; ambient temperature	CO ₂ /H ₂	simple operating scheme; low capital cost	high operating cost; expensive solvent
physical absorption	Purisol	N-methyl-pyrrolidone	350 psi CO ₂ ; –15–0 °C	CO ₂ /H ₂	low volatility	high capital cost
physical absorption		ionic liquids	250–850 psi; ambient temperature	CO ₂ /N ₂	low energy for regeneration	low work capacity; high production cost

and Purisol are four commercial technologies for physical solvent driven CO₂ capture. If one wants to apply these technologies for postcombustion CO₂ capture, the flue gas must first be given an energy-intensive pretreatment. Because of the low volatility, high thermal stability, and nonflammability, ionic liquids (ILs) are being increasingly viewed as a suitable alternative to the above organic physical solvents. ILs, including a broad category of salts that can dissolve gaseous CO₂, are stable at temperatures up to several hundred degrees centigrade.¹² As shown in Table 1, the low working capacity is traditionally associated with basic ILs. Therefore, functionalized ILs (through the incorporation of functional groups into basic ILs) have been developed to enhance the CO₂ affinity.¹³

Challenge. Although a diverse range of chemical-absorption materials have been explored, such material-based separations, primarily driven by temperature swing, are reliable but not necessarily optimal. Furthermore, the expensive production cost of absorbents, especially the high manufacturing costs of ILs, prohibits such processes to be scaled-up to a commercial level. In the future, the following issues need to be further investigated:

- In-depth understanding of the chemisorption mechanisms of solvent-based CO₂ capture is required to improve the capture performance and reduce the inherent regeneration cost.
- The long-term stability, high CO₂ purity rate, and tolerance to impurities should be significantly enhanced through development of new chemical-absorption-based capture technologies.
- The fundamental reaction mechanism and kinetics of the functionalized ILs reacting with CO₂ should be elucidated.
- Particular attention should be paid to enabling commercial absorbent production in bulk quantities at reasonable prices.

Several solvents have been used in small/medium-scale industrial sectors and are being tested in large-scale CO₂ capture demonstration plants such as power plants and hydrogen production facilities;¹⁴ however, it is unlikely that conventional solvents can deal with the daunting challenges involved with CO₂ capture. Fundamental research and innovations on other types of material should still be carried out in parallel to make CO₂ capture technologies more feasible on a large scale.

2.1.2. Solid Sorbents. Novel sorbent materials with specifically designed structures, which allow them to bind selectively CO₂ from gas mixtures and remove/concentrate it in a controlled fashion such as pressure, temperature, or vacuum swing adsorption cycles, have huge potential. As shown in Figure 4, solid sorbents presently utilized for CO₂ capture include activated carbon, metal oxides, zeolites, alkaline, amine-enriched

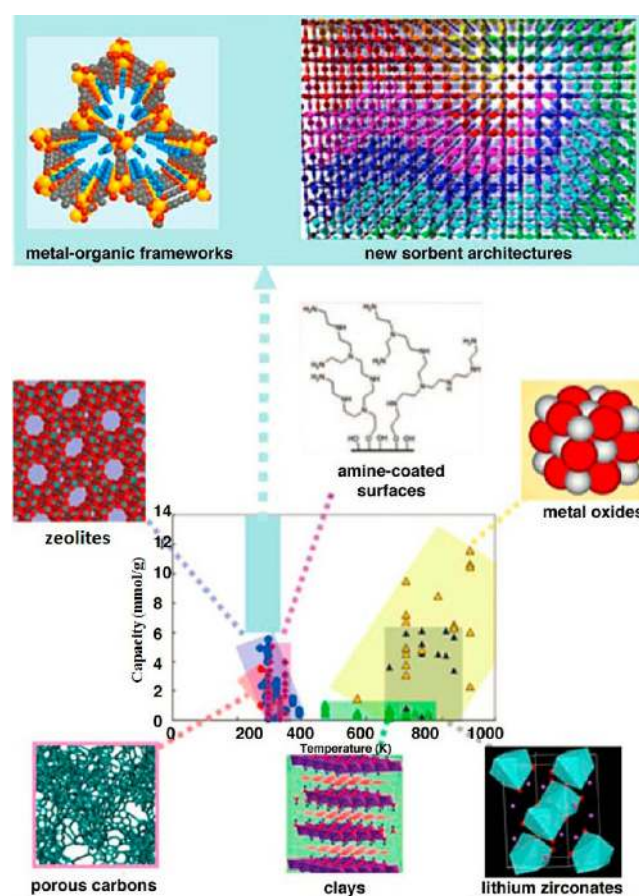


Figure 4. Potential solid sorbents and the relevant relationships between capacity and temperature (adopted from ref 15).

solids, lithium zirconates, MOFs, and COFs. These technologies, i.e., molecular sieving, physisorption, and chemisorption, involve the following main operations:

- The solid sorbents remove CO₂ from gaseous streams by adsorbing it on the solid surface.
- The CO₂-rich solid sorbents are then regenerated through pressure, temperature, and vacuum swing systems to liberate the CO₂.
- The CO₂ uptake capacity, selectivity, stability, and regenerability are main adsorption properties of a solid sorbent.

Rather than performing a comprehensive review of all possible solid materials, we focus this discussion only on the top adsorption materials to highlight recent advances and to point out obstacles that impede their large-scale implementation. More comprehensive reviews on solid sorbents driven CO₂ capture have been reported by others.^{7,16–18} Table 2 outlines the main solid-sorbent-based technologies along with the advantages and disadvantages associated with their use.

Zeolites. Zeolites are crystalline aluminosilicates with well-defined porous structures. The metal atoms in zeolites are surrounded by four oxygen atoms in tetrahedron geometry. The crystalline materials stack into regular arrays with the formed channels making them promising potentials for CO₂ capture. In general, the gaseous stream needs to be cooled below 100 °C and the impurities also need to be removed when utilizing zeolites for CO₂ capture.

CO₂ adsorption on zeolites with fast kinetics is categorized as reversible physisorption that is governed by a thermodynamic equilibrium process. Actually, irreversible chemisorption on the zeolite surface also occurs.⁹ The zeolite topology and composition (Si/Al and extra framework cations) determine the equilibrium and kinetic properties. Low Si/Al ratios and the extra framework cations are favored because of the stronger electrostatic interactions with CO₂.¹⁹ Prior research activities have revealed that zeolites demonstrating very high selectivity usually have special structural features such as double-crankshaft chains and double eight-ring units.²⁰ Several zeolites, such as X and Y Faujasite systems, 4A, 5A, and 13X, have been extensively investigated.^{21,22} The CO₂ adsorption capacity of zeolites is substantially higher at ambient temperature than at elevated temperature. Generally speaking, the CO₂ adsorption capacity under a fixed pressure increases significantly with a slight decrease of the adsorption temperature. Although zeolites can exhibit superior performance under certain conditions, the dominant challenges that hamper their large-scale practical deployment are as follows.

- Poor adsorption capacity and stability in the presence of moisture and other impurities.
- Energy and time-intensive temperature swing approach is required to reach complete regeneration necessary for maintaining the adsorption capacity.

Metal Organic Frameworks (MOFs). As a result of the attractive structural properties given in Table 2, MOFs show strong potential for selective CO₂ capture under a variety of scenarios.²³ Laboratory-scale investigations have shown that MOFs are suitable for capturing CO₂ under elevated pressure scenarios such as natural gas purification and coal gasification, whereas at low CO₂ partial pressures, traditional zeolites and activated carbons perform better than MOFs.²⁴

Since the first class of MOFs have been synthesized,²⁵ diverse strategies, including pore-size control, open metal sites, incorporation of polar functional groups, and the introduction of

Table 2. Main Solid-Sorbent-based CO₂ Capture Technologies and Relevant Advantages/Disadvantages

solid sorbent	optimal working condition			main application	advantage	disadvantage
	mechanism	pressure (psi)	temperature (°C)			
activated carbon	physisorption	1.45–145	25–75	CO ₂ /CH ₄	cheap raw materials; rapid carbonation kinetics; low desorption temperatures	low CO ₂ capacity at mild conditions
zeolite	physisorption; chemisorption	1.45–14.5	0–100	CO ₂ /N ₂	fast adsorption kinetics; high CO ₂ capacity at mild conditions	expensive pretreatment; poor properties under high temperature
MOF	chemisorption	high	low	CO ₂ /CH ₄ CO ₂ /H ₂	high surface area; tailorable pore metrics; high density of active sites; adjustable chemical functionality; huge and accessible pore volumes	unclear regenerability; expensive synthesis route; low CO ₂ capacity under mild conditions
amine-enriched solid	physisorption; chemisorption		25–75	CO ₂ /N ₂	negligible impact of pressure; positive impact of vapor fast adsorption kinetic; high CO ₂ adsorption capacity	inferior stability after multiple cycles; sensitive to impurities; long time to reach equilibrium
	physisorbed amine-enriched silica solid					thermal degeneration; irreversible reactions with acid gases
	covalently tethered amine-enriched silica solid					
	amine-grafted organic				rapid mass transfer; fast adsorption kinetic; high CO ₂ adsorption capacity	unclear stability properties; fail to work under high temperature

alkali-metal cations have been employed to ameliorate the CO₂ capture performance of MOFs.⁷ Direct assembly and postsynthesis modification are two methods to enable precise tuning of pore size and creation of desired functionalities.²⁶ Replacing coordinated solvent molecules with highly polar ligands is regarded as an efficient strategy to improve adsorption properties. To date, heterocycle derivatives, aromatic amine derivatives, and alkylamine bearing frameworks have been used to functionalize MOFs. Multivariate MOFs fabricated by incorporating heterogeneity linkers into the same crystal can offer very high selectivity toward CO₂ capture.²⁷ CO₂ selectivity, capacity, and uptake can also be enhanced through rare-earth metal promoted open metal sites and proximal highly localized charge density.²⁸ Apart from the modification methods, investigation of the dynamics of the adsorbed CO₂ within the MOFs over a wide range of temperature/pressure is another important topic to reveal the CO₂–host and CO₂–CO₂ interactions.²⁹ Furthermore, optimized reaction conditions (temperatures, solvent compositions, and reaction times) can also greatly enhance the characteristics of MOFs for CO₂ capture.

To accelerate the deployment of MOFs for large-scale CO₂ capture, realistic operating conditions should be adequately taken into account. Moisture is traditionally one of the main limiting factors in practical application of most MOFs.³⁰ The presence of impurities in the gaseous stream limits the CO₂ selectivity and adsorption capacity of MOFs.³¹ Strategies that can enhance CO₂–host interaction while requiring low energy for regeneration are needed.³² Ideally, the desirable materials for CO₂ capture must be structurally robust, be readily available, exhibit scalable properties, and reasonable manufacturing costs. The following issues, including the aforementioned sensitivities to water vapor and impurities, still require significant research activities to enable the use of MOFs for CO₂ capture on a large scale, especially for postcombustion scenarios.

- MOFs showing extraordinary adsorption characteristics at mild conditions are rare.
- Current MOF synthesis routes cannot be scaled up for large-scale applications in an environmentally friendly manner due to the use of expensive and often toxic solvents.
- Desorption properties of MOFs and the effect of multiple adsorption/desorption cycles on long-term stability need to be better understood.
- The synthesis and characterization of MOFs with expensive linkers has been tested only in laboratory scale (milligram scale).

Amine-Grafted Solid Materials. Solids impregnated or tethered by active groups, such as aqueous solutions of amines, are another class of widely researched materials. The key idea behind synthesizing such amine-grafted solid materials is to combine the advantages of both aqueous solutions and solid materials to maximize the sorption properties. MCM-41 impregnated by polyethylenimine is the first of such type of adsorbent.³³ Since then, numerous amine-functionalized silica materials have been synthesized for postcombustion and capture of CO₂ from ambient air.³⁴ Unlike the aforementioned aqueous solutions, these functionalized solids require lower temperatures and less energy inputs for regeneration. Compared to traditional solids, they possess higher CO₂ selectivity and CO₂ adsorption capacity.

Physisorbed amines impregnated adsorbents and covalently tethered amine adsorbents are two traditional types of

amine-grafted silica-based solids. The former usually shows inferior stability in the presence of impurities and multiple cycles. Hyperbranched aminosilica (HAS) material³⁵ is one example of the covalently tethered amine adsorbents that can be fully regenerated through repeated adsorption/desorption cycles. Furthermore, a group of HAS adsorbents with different organic loadings have been prepared to elucidate the synthesis–structure–characteristic relationships.³⁶ The adsorption characteristics of these materials heavily depend on both the selection of organic solutions and the corresponding density.³⁷ Indeed, the stability property is inherently affected by the alkyl linker and also by impurities.^{38–40} In addition, there are a variety of organic supported amines including amine-grafted porous carbons, organic resins, and polymers. Among these amine-grafted organics, amine/silica/polymer composite hollow fiber adsorbents have received much attention.⁴¹ For example, mesoporous silica/cellulose acetate hollow fibers infused with 3-aminopropyltrimethoxysilane (APS), hollow fibers infused with poly(ethylenimine) (PEI), and poly(amide-imide) (PAI)/silica/PEI–glycerol sorbents have been synthesized and studied in detail.⁴²

Because of the reasonable mass transfer, adsorption kinetics, negligible influences of CO₂ partial pressure, and enhanced CO₂ capacity at low temperature, the amine-grafted solids are particularly desirable for postcombustion CO₂ capture. Nevertheless, prior to the industrial adaptation of these amine-functionalized support materials for CO₂ capture, several obstacles need to be overcome first.

- The effect of scalability, tolerances to impurities, and long-term stability of amine-grafted solid sorbents for practical application are still unclear.
- The intensive energy requirement associated with traditional pressure swing adsorption (PSA) and the long regeneration time linked to temperature swing adsorption (TSA) raise questions regarding cost and desorption efficiency.
- The environmental impacts when manufacturing and deploying amine-grafted solid sorbents on a large scale are unknown.
- The optimal arrangement of amine-grafted solid driven CO₂ capture configurations required for matching the capture targets.

Other Solid Sorbents. There are many other solid sorbents^{43,44} showing potential for CO₂ capture such as carbon-based adsorbents, molecular porous, graphene base porous, covalent organic polymers, hyper-cross-linked polymers, porous aromatic frameworks, and conjugated microporous polymers. For instance, activated carbons are attractive for high pressure precombustion CO₂ capture as a result of their high thermal stability, favorable adsorption kinetics, and large adsorption capacity. However, activated carbons may not be suitable for postcombustion CO₂ capture due to low CO₂ capacity/selectivity at mild conditions and negative impacts of NO_x and SO_x. Irrespective of which kind materials are used, two main issues need further investigations.

- The recyclability of these materials needs to be clearly demonstrated.
- The environmental impacts stemming from the production of these organic materials need to be established.

Challenge. With the aim of large-scale implementation, viable solid materials should possess the following properties: desirable adsorption capacity and selectivity; reasonable adsorption

Table 3. Summary of Main Membrane-based CO₂ Capture Technologies

membrane type			selectivity				
		mechanism	CO ₂	H ₂	permeation	resistance to impurities	
inorganic	metal	solution-diffusion		✓	low	excellent	
	ceramic	solution-diffusion	✓	✓	low	moderate	
		chemical reaction	✓				
	zeolite	adsorption-diffusion	✓	✓	high	excellent	
	MOF				moderate	moderate	
	ZIF				high	moderate	
	silica	amine-grafted	adsorption-diffusion	✓		low	moderate
		amine-functionalized				high	
		stabilized	molecular sieving		✓	high	excellent
			activated diffusion				moderate
polymeric		solution-diffusion	✓	✓	low	poor	
mixed matrix		solution-diffusion	✓	✓	moderate	poor	
facilitated transportation		solution-diffusion	✓		high	moderate	

kinetics; mild conditions for regeneration; superior tolerance to impurities; low material cost; preferably a green synthesis route and excellent long-term stability during multiple controllable adsorption/desorption cycles. Significant research may be required to bridge the gap between the fundamental scientific predictions and the requirements of large-scale industrial applications. Two key questions that should be investigated further are

- What fundamental research is needed to overcome the uncertainties of economic and environment performance for large-scale manufacture of solid sorbents?
- What kind of structures and compositions of solid sorbents can guarantee the desirable chemical/physical characteristics when applied to large-scale plants?

2.1.3. Membranes. Membranes fabricated using permeable or semipermeable materials are also candidates for selective CO₂ separation, which follows chemical/physical mechanisms including solution-diffusion transport, molecular sieving, and Knudsen diffusion.^{45,46} In general, membrane driven systems possess a number of key merits:

- Low energy usage and operational simplicity.
- Compactness, no use of hazardous chemicals with disposal issues.
- Easy installation of modules into existing infrastructures, and no moving parts.

CO₂ permeability and selectivity are two important parameters for polymeric membranes. Membrane separation systems have been commercially installed for removing CO₂ from natural gas streams. However, challenges exist in applying membranes to postcombustion capture scenarios due to the low pressure of such gaseous streams. Currently, inorganic membranes, organic membranes, mixed matrix membranes, and composite membranes are being extensively assessed for application in scenarios with low CO₂ partial pressure and H₂ capture. Table 3 offers the mechanism, selectivity, and permeability of the main membrane-based capture technologies.

Inorganic Membranes. For the CO₂ capture from flue gas streams, inorganic membranes, typically composed of either porous or nonporous materials such as ceramic, metal oxide, graphene oxide, metallic, molecular sieves, silica, zeolites, and MOFs (ZIFs), are employed.^{47,48} In general, inorganic membrane driven capture is mainly promoted by molecular sieving, adsorption-diffusion, or solution-diffusion. Because of similar sizes for CO₂ and N₂ molecules as well as low permeance,

molecular sieving does not exhibit sufficient CO₂ separation capability. Improved membrane intergrowth, controlled thickness and size, and reduced concentration of “non-selective pores” are three particular obstacles that need to be overcome to achieve higher and acceptable CO₂ separation capability and thereby, industrial application of membrane-based technologies. Among existing inorganic membranes, zeolite membranes are perhaps the most widely investigated candidates for applications in precombustion⁴⁹ and postcombustion⁵⁰ CO₂ capture. The extremely high porosity and high surface areas of MOFs may lead to high CO₂ permeance with MOF membranes.⁵¹

Although, experimental studies have demonstrated that certain inorganic membranes exhibit outstanding characteristics, including permeance and chemical/thermal stabilities, large-scale applications of inorganic membranes for CO₂ capture, have not been possible due to the following issues:

- Questions regarding the long-term resistance, stability and reproducibility.
- The fabrication routes for inorganic membranes are expensive and difficult to scale up.

Polymeric Membranes. Because of excellent mechanical properties as well as the low fabrication costs, polymeric membranes⁵² hold great potential for postcombustion⁵³ and precombustion CO₂ capture.⁵⁴ Gas transport through polymeric materials is promoted by a partial pressure driving force based on solution-diffusion mechanism. The amount of free volume within the framework and the nature of the permeant species determine the permeability. Selectivity is obtained by the diffusion through the dense polymeric matrix and the differences in solubility of specific gases within the polymeric membrane. Traditional polymeric membranes unfortunately demonstrate low CO₂/N₂ selectivity. Desirable polymeric membranes for postcombustion CO₂ capture should display thermal/physical stability, resistance to contaminants, and reasonably balanced permeability and selectivity at low pressure drop. Increasing solubility, selectivity, and the chain stiffness along with the interchain spacing/free volume enhancement are two approaches to break through the famous Robeson’s upper bound⁵⁵ on the selectivity–permeability balance.⁵⁶ Following the latter approach, polymers of intrinsic microporosity (PIMs), a class of glassy polymers, can create a large amount of free volume.⁵⁷ For example, poly(1-trimethylsilyl-1-propyne) may be the most known permeable polymer;⁵⁸ however, its unfavorably high interchain spacing leads to poor diffusivity and selectivity. Therefore, considerable modifications

Table 4. Selection of Technologies for CO₂ Capture from Ambient Air

material	advantage	disadvantage
alkaline solution	cheap material; high CO ₂ selectivity	energy-intensive regeneration
traditional solid physisorbent	high thermal stability	negative impact of moisture
chemisorbent	high adsorption capacity under high temperature	huge heat requirements for desorption
solid supported amine	high tolerance to moisture; low energy requirement for regeneration	require hours to achieve saturation
amine-grafted MOF	fast kinetics; high CO ₂ capacity	unclear stability; sensitivity to moisture; expensive synthesis routes

have been studied to improve the performance of PIMs for CO₂ capture.⁵⁹

It should be mentioned that to date, commercially available membranes for CO₂ capture in natural gas sweetening are based mainly on polymeric materials. As given in Table S1,⁶⁰ the CO₂/N₂ selectivity associated with the majority of these commercial membranes is normally in the range of 20–30 and the pressure-normalized CO₂ flux is fairly low. Data given in the last row of Table S1 indicate that the hydrophilic polymer-based Polaris membrane system, developed by MTR, has achieved tremendous improvement in balancing the CO₂ permeability and CO₂/N₂ selectivity.⁶¹ Recently, such a promising technology for economically capturing 90% of the CO₂ emitted from an 880 megawatt pulverized coal power plant has begun pilot-scale evaluation.⁶² In conclusion, the challenges for scaling-up polymeric membranes for large-scale deployment can be summarized in three main aspects.

- Polymeric membranes are very sensitive to impurities.
- Polymeric membranes need to balance appropriately CO₂ permeability and selectivity.
- The scalability and the environmental impacts of the fabrication routes for polymeric membranes need to be established.

Mixed Matrix Membranes. Mixed matrix membranes (MMMs),⁶³ which combine a bulk continuous polymer phase and a homogeneously distributed inorganic discrete phase, are another type of promising candidates because they can enable synergistic enhancements in CO₂ permeability and selectivity as well as improvements in mechanical and thermal stability.

Therefore, the optimal selection of the polymer and inorganic phase will play a key role. Desirable polymer candidates can guarantee good adhesion between the polymer and inorganic particles. In general, polysulfones, polycarbonates, polyarylates, poly(arylketones), poly(arylethers), and polyimides, block copolymers have been employed. Porous and nonporous materials can be used as inorganic fillers.⁶⁴ It should be emphasized that porous candidates for the inorganic phase must possess large pores to avoid molecular sieving effects.⁴⁶ Among potential candidates, such as zeolites,⁶⁵ ZIFs/MOFs,⁶⁶ carbon nanotubes,⁶⁷ silica,⁶⁸ and metal oxides,⁶⁹ zeolites are the most common inorganic candidates as filler for the fabrication of MMMs. Compared with zeolite, MOFs can more easily control the interface morphology between two phases, which in turn affects the stability of MMMs.⁷⁰ In addition, the technology for MMMs fabrication is another vital aspect. For instance, the crystals of MMMs generated by in situ crystallization can offer better characteristics than those MMMs whose preformed nanocrystals are dispersed by cocasting with the polymer.⁷¹ To promote the implementation of MMMs on a large scale, the challenges listed below require considerable further research.

- The fabrication process for MMMs is very expensive and cannot be easily scaled up.

- The physical aging evaluation over long-term operation needs to be established.
- The CO₂ capture performance of MMMs in the presence of aggressive chemical contaminants needs to be established.

Facilitated Transportation Membranes. Liquid-supported membranes or enhanced ion-exchange membranes are two forms of facilitated transport membranes. Superior stability, mechanical properties, and high CO₂/N₂ and CO₂/H₂ selectivities make them promising candidates for separating CO₂ from both high-pressure and low-pressure gaseous streams.

The main mechanism associated with the facilitated transportation membranes is as follows: the CO₂ molecule selectively and reversibly reacts with carrier molecules in the membrane while allowing other nonreactive gas components to transport following solution-diffusion mechanism. That is, CO₂ reacts with primary/secondary amines to form a carbonate ion. The reaction product then diffuses through the membrane and releases CO₂ on the permeate side of the membrane with a relatively low CO₂ partial pressure. Clearly, the carriers determine the CO₂ capture performance of such composite membranes. Carriers with low reaction rate, low absorption capacity, volatility, and poor stability may be undesirable. Hydrophilic blends of cross-linked poly(vinyl alcohol) (PVA)⁷² and polyallylamine (PAA),⁷³ polyamidoamine (PAMAM) dendrimers,⁷⁴ and blends of pure PVA with polyethylenimine (PEI) or polyvinylamine (PVAm) as carriers have been evaluated. For instance, polyvinylamine (PVAm) fixed-site-carrier (FSC) composite membrane demonstrates remarkable properties with a CO₂ permeability greater than 1000 GPU and a CO₂/H₂ selectivity larger than 200 at 120 °C.⁷² Before these membranes can be used, the following issues need to be studied.

- The relationship between separation performance and material properties such as cross-linking degree and membrane thickness.
- The CO₂ capture performance and durability in harsh operating environments.
- The economic performance and environmental impacts associated with the manufacturing process for transportation membranes.

Challenge. Inorganic membranes and MMMs are still far from their large-scale utilization for CO₂ capture. High CO₂/H₂ selectivities associated with several polymeric membranes promise a competitive edge, compared to conventional technologies for capturing CO₂ from high-pressure gaseous streams. Resulting from the extremely low CO₂/N₂ selectivities and permeances, these membranes are, however, not suitable for postcombustion CO₂ capture. A lower threshold of CO₂/N₂ selectivities for membranes is suggested at 200 for postcombustion CO₂ capture.⁷⁵ As illustrated by Figure 5a, the majority of polymeric and composite membranes fails to meet this target. Although for those membranes with the CO₂/N₂ selectivities

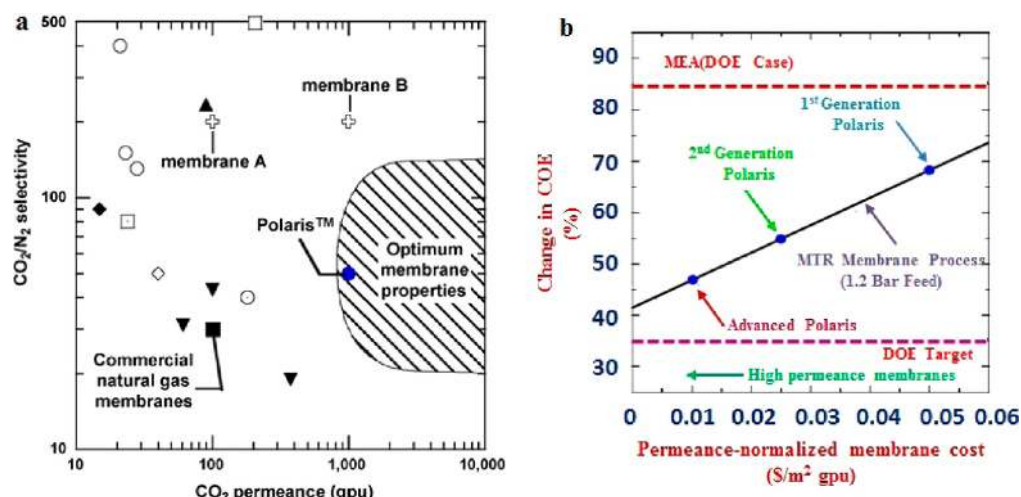


Figure 5. Comparisons of membrane performance for flue gas postcombustion CO₂ capture and relationship between the normalized membrane cost and changing in COE (adopted from refs 53 and 76).

higher than 200, their CO₂ permeances are very low, which would require extremely high membrane areas for achieving the set capture rate. In other words, improving permeance can reduce the membrane area and in turn cut down the cost and size of the system. The shaded area in Figure 5a depicts the optimal membrane properties. Currently, several polymeric and facilitated transport membranes are under pilot-scale test. However, as shown in Figure 5b, there are still considerable opportunities for improving the separation properties to satisfy established CO₂ capture targets even for the advanced MTR Polaris technology. In the future, several key theoretical and engineering issues must be addressed.

- The relationships between the membrane morphology/composition and separation properties under industrial conditions must be established.
- A reliable route for module development is needed.
- Large-scale membrane fabrication processes that are robust and environmentally benign.

2.1.4. Summary. Significant progress on solid sorbents and membranes as alternatives to conventional MEA absorption materials for CO₂ capture has been achieved. However, MOFs, inorganic membranes, and MMMs are still far from large-scale deployment for CO₂ capture, especially for postcombustion CO₂ capture. Amine-grafted sorbents, polymeric and facilitated transport membranes show high potential for future deployment on a large scale. Although, CO₂ capture by chemical absorption with aqueous solutions continues to be, in certain cases, the most viable and practical option, it does require energy-intensive regeneration. Solid sorbents and membrane-based technologies can surpass the performance of chemical absorption and therefore replace this approach once the following issues are addressed:

- CO₂ capture/separation performance under the presence of impurities needs to be improved.
- Long-term membrane durability associated with impurities need to be established.
- Long-term stability linked to solids under influence of impurities and considerable CO₂ adsorption/desorption cycles need to be controllable.
- Smart, scalable, environmentally benign, and cost-effective approaches for manufacturing solids and membranes need to be determined.

2.2. Capturing CO₂ from Ambient Air. The current CO₂ level in the atmosphere is a major concern and emission reductions through CO₂ capture from stationary points will most likely not be enough to address the climate change issue. Capturing CO₂ directly from ambient air has therefore become a very critical area of research.^{77–79} Anthropogenic CO₂ capture from air is very challenging because of thermodynamic limitations resulting from the extremely dilute CO₂ concentrations, and the energy cost for driving large volumes of air through a capturing process. Classical CO₂ separation processes such as cryogenic distillation and membrane-based separation are not economically competitive. During the past several years, numerous contributions have been devoted to evaluating different approaches for CO₂ capture from the ambient air. Table 4 presents a selection including, use of alkaline solutions, traditional solids, amine-grafted oxides, and MOFs.

2.2.1. Alkaline Solutions. Alkaline-solution-based technologies are well-investigated and incorporate chemical absorption such as LiOH/NaOH/KOH/Ca(OH)₂ scrubbing to produce metal carbonates with CO₂. The produced metal carbonate solution is recycled back to the hydroxide-based solution to establish a cyclic process. The captured CO₂ can be further sequestered or utilized as C₁ chemical feedstocks. For these alkaline solutions, a wide spectrum of devices such as packed columns, open towers, and pools, where CO₂ would react with hydroxide-based solutions, are traditionally required.⁸⁰ Although these alkaline solutions make the capture process cheap, expensive energy and processing costs associated with the expensive endothermic regeneration are severe obstacles.

2.2.2. Traditional Sorbents. Traditional solid sorbents may also be utilized for capture of CO₂ from ambient air. It should be pointed out that zeolites and activated carbon, which have been considered for the postcombustion/precombustion CO₂ capture, may not be the top alternatives for CO₂ capture from ambient air as large amounts of moisture may impede the selectivity toward CO₂ at atmospheric pressure. In addition, these physisorbents have low CO₂ adsorption capacities because of low heat of adsorption.⁸¹ Compared to physisorbents, chemisorbents such as calcium- or sodium-based oxides require cheap heat sources and innovative equipment to lower the overall cost.

2.2.3. Amine-Grafted Oxides. Steep adsorption isotherms and vapor insensitivity under ambient conditions are two important

criteria for evaluating potential alternatives to traditional solid sorbents. Solid supported amines/polyamines are promising materials for capture of CO₂ from ambient air. The main principle behind solid supported sorbents is to adjust the amine loading to improve CO₂ adsorption capacity under ambient conditions. Triggered by an appropriate ion-exchange resin functionalized with quaternary ammonium ligands,^{82,83} various modifications on solid sorbent supports and compositions have been investigated. Silica,^{84,85} alumina,⁸⁶ and carbon^{87,88} as supports along with L-lysine,⁸⁹ allylamine,⁹⁰ and in particular polyethylenimine^{91,92} as deposited compositions have been analyzed for their efficacy as adsorbents for capture of CO₂ from ambient air. These amine-functionalized oxides have been found to show superior CO₂ adsorption capacity and stability after multiple regeneration cycles under low values of relative humidity. Nevertheless, a majority of the studied materials frequently require several hours to achieve saturation due to their slow adsorption kinetics.

2.2.4. Amine-Grafted MOFs. Most of the MOFs investigated so far, with or without unsaturated metal centers or/and functionalized ligands, have not been found to offer significantly improved CO₂ capture performance at relatively low CO₂ partial pressure. Combining MOFs with amine/polyamines, to some extent, might be suitable for capturing CO₂ from ambient air. MOF modification by grafted amines can exploit the formation of a strong chemical bond to enhance the affinity toward CO₂ and a correspondingly high CO₂ selectivity.⁹³ Indeed, pore-size control coupled with suitable energetics of favorable electrostatics from an array of inorganic anions for MOF can also afford superior CO₂ uptake in the context of capture from ambient air.⁹⁴ For example, ethylenediamine has been used to modify the Mg-MOF-74 to enhance the CO₂ adsorption capacity.⁹⁵ Subsequently, a combination of the expanded iso-structure of Mg-MOF-74 with *N,N*-dimethylethylenediamine grafting exhibits high selectivity and fast kinetics for adsorbing CO₂ from air.⁹⁶

2.2.5. Other Technologies for Capture of CO₂ from Ambient Air. Besides the above-discussed approaches for CO₂ capture, membrane-based technologies have begun to receive attention. Most recently, an ion-exchange resin-based membrane, where the positive anions in the resin are responsible for attracting CO₂, has been designed.⁹⁷ This material is claimed to be working best in warm and dry climates. However, these approaches are still in their very early stage, and their capital cost and long-term efficiency are unknown.

2.2.6. Summary. It has been reported that given identical economic conditions with respect to facilities, the operating cost of CO₂ capture processes from ambient air would be higher than the stationary point-source capture processes.⁹⁸ Several contributions have questioned their economic viability and offered different scales of rough net operating cost of air CO₂ capture regarding the utilization of hydroxide, ion-exchange resin, and amine-functionalized adsorbents.^{80,99–102} Nevertheless, breakthroughs in the following issues can lead to achievement of large-scale deployment of cost-effective air capture of CO₂, although there is still a long way to go before this becomes reality.

- Identification of relationships between CO₂ selectivity/work capacity and energy requirements for regeneration.
- The long-term stability during cyclic CO₂ adsorption/desorption operation under ambient conditions.
- A comprehensive database establishing relationships among material characteristics, operating conditions and CO₂ capture performance.

- The evaluation of superior materials predicted by laboratory-level experiments on pilot and even demonstration plants.
- The assessment of economic viability and environmental impacts of air capture systems from a systems engineering perspective.
- The coordination of different disciplines such as material/chemistry scientists and process engineers.

2.3. Conclusions on Technologies for CO₂ Capture. The development of thermodynamically efficient and scalable CO₂ capture technologies is one of the greatest current challenges for scientists and engineers. A wide range of technologies have been proposed and developed for capturing CO₂ from stationary points and ambient air. The above sections have briefly discussed the key progress associated with the solvents, solid sorbents, and membranes. As shown in Table S2, each material has several advantages but also demonstrates serious disadvantages. Those materials, which are suitable for CO₂ capture from stationary points, may not be favored for air CO₂ capture. Similarly, those materials, which work well in natural gas purification and high-purity H₂ production, may not be suitable for capturing CO₂ from flue gas emitted from coal-based power plants. Only significant advancements in both stationary CO₂ capture and ambient air CO₂ capture can optimally address the question of climate change. Material/chemistry scientists and process engineers must effectively collaborate to explore optimal and reliable CO₂ capture technologies that can be implemented on a large scale with minimum cost and energy requirements as well as minimum negative environmental impacts.

3. CO₂ CONVERSION TECHNOLOGIES

A full-scale power plant with an integrated carbon capture and storage (CCS) facility would cost much more than a traditional coal power plant without the CCS implementation. The reasonable utilization of the captured CO₂, to some extent, can offset the high operating and capital cost for implementing the capture facility. Indeed, CO₂ should not be considered as a waste product but rather as a very attractive, nontoxic, and plentiful C₁ building block for producing value-added products through a great number of C–C/H/C–O/C–N bonds formulation routes.^{103–107} However, those reactive substrates including nitrogen-containing compounds and epoxides for reducing CO₂ to commodity and specialty chemicals through the formulation of new C–O and C–N bonds are outside the scope of this paper.

Because around 6.8 gigatonnes of carbon in the form of recyclable CO₂ is produced each year at various point sources,¹⁰⁸ the best route is to transform CO₂ into liquid transportation fuels, aromatics, olefins and their derivatives, which are currently produced from petroleum, with significant energy storage. The subsequent sections mainly focus on these topics as illustrated by Figure 6. Accordingly, biochemical/biological, electrochemical, photochemical, and traditional catalytic routes such as Fischer–Tropsch (F-T) synthesis and methanol synthesis are touched upon.

3.1. Syngas Production from CO₂. As a universal intermediate, syngas can be converted to numerous value-added products via methanol synthesis and F-T synthesis. Regarding these indirect CO₂ conversion routes, the most important issue is the reduction of thermodynamically stable CO₂ to syngas through a cost-effective and high-efficiency conversion route. The first of such promising routes is H₂

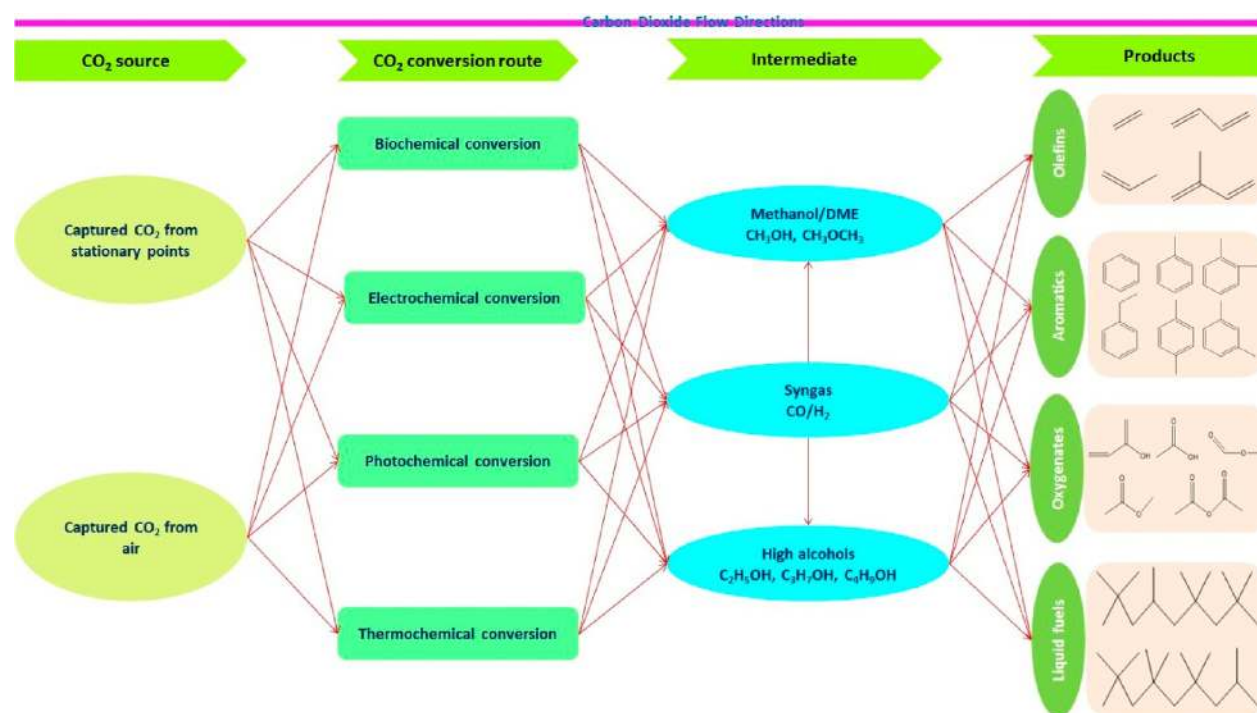


Figure 6. Summary of discussed CO₂ conversion routes and product distribution.

Table 5. General Summary of Syngas Production from CO₂

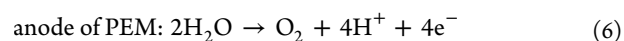
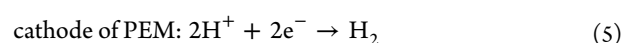
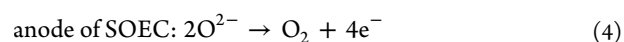
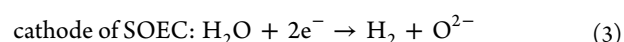
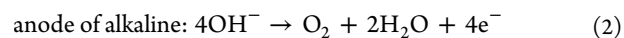
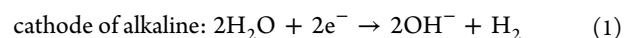
	technology	supplementary pathway	advantage	disadvantage
H ₂ driven syngas production	natural gas steam reforming	RWGS	mature technologies	huge CO ₂ emission
	biomass gasification			
	coal gasification			
reforming	renewable energy driven H ₂ O splitting	cheap and abundant CH ₄ available	environmental benign	low efficiency; high capital cost; immature technologies
	dry reforming (CO ₂ +CH ₄)			
	bireforming (CO ₂ +O ₂ +CH ₄)			
	bireforming (CO ₂ +H ₂ O+CH ₄)			
CO ₂ splitting driven syngas production		WGS	environmental friendly	poor efficiency; high capital cost; immature technologies

production followed by the reverse water gas-shift reaction (RWGS). Second is the reaction of CO₂ with CH₄. The third alternative involves the splitting of CO₂ followed by WGS. Table 5 lists the general merits and drawbacks of the three routes.

3.1.1. Hydrogen Production. Available routes for producing H₂ include water electrolysis, water thermolysis, water thermochemical splitting, water photochemical splitting, natural gas reforming, biomass gasification, and coal gasification.¹⁰⁹ For reduction of CO₂, the renewable-energy-based water splitting process for H₂ production could become a desirable pathway from environmental and sustainability viewpoints.¹¹⁰ Cost-effectiveness and energy efficiency are two key drivers for implementing such sustainable technology in large-scale CO₂ reduction. Unfortunately, most existing water splitting technologies are not yet ready to be deployed as a result of the disadvantages summarized in Table 6.

Water electrolysis for splitting water into hydrogen and oxygen essentially is an endothermic electrochemical reaction. Cathode, anode, and electrolyte are three components for an electrolyzer.

Alkaline electrolyzers, solid-oxide electrolyzer cells (SOEC) and polymeric electrolyte membrane (PEM) electrolyzers are three commercially available electrolyzers. The detailed chemistry mechanisms of these three electrolyzers are given by eqs 1–6.



Alkaline Electrolyzer. An alkaline electrolyzer is a considerably robust technology, where an aqueous alkaline electrolyte is traditionally employed. Cheap nonprecious metals or oxides (such as stainless steel and nickel) are used as cathodes of

Table 6. Summary of Solar Energy Driven Water Splitting

technology	pressure (bar)	temperature (°C)	system efficiency (%)	solar-to-H ₂ efficiency (%)	advantage	drawback
alkaline electrolysis	25–30	80–90	63–73	10	commercial technology; low capital cost	low current density H ₂ /O ₂ mixing
PEM electrolysis	<85	<100	56	8.5	high current density; compact design H ₂ /O ₂ produced separately; small mass-volume characteristic	high capital cost; expensive metal catalyst
solid oxide electrolysis	30	500–850	85–90	12	high electrical efficiency; non-noble catalyst H ₂ /O ₂ produced separately	brittle ceramics
photoelectrochemical	1	25		12	high solar efficiency H ₂ /O ₂ produced separately	degradation
photocatalytic	1	25		0.2	simple module	poor solar efficiency H ₂ /O ₂ mixing
thermolysis	1	2200		1–2	simple module	poor material stability H ₂ /O ₂ mixing; high radiative losses
thermochemical		>700	40	18	high energy efficiency; H ₂ /O ₂ produced separately	high capital cost; complex process design

commercial alkaline electrolyzers, whereas anodes utilize Ni coated by metal oxide. Significant efforts have been devoted to finding novel electrocatalysts to overcome the poor long-term electrochemical activity and durability associated with existing commercial cathodes.^{111–114} High electrical conductivity, superior corrosion resistance, and minimum overvoltage are three fundamental requirements for significantly enhancing the performance of an alkaline electrolyzer.

PEM Electrolyzer. PEM electrolyzers are composed of precious-metal-electrocatalysts-based electrodes and smart cross-linked, perfluoro-sulfonated acid polymer membranes. State-of-the-art PEM water electrolyzers can now operate at 1 A·cm⁻² with a higher-heating-value (HHV) efficiency close to 75–80%.¹¹⁵ Expensive platinum-group-metals (such as Pt, Rh, Ir, Ru) electrocatalysts are usually required to ensure that the PEM electrolyzer works well under the acidic environment. However, these rare and expensive metals cannot guarantee the sustainability of this process. Various modifications of electrocatalysts and polymeric membranes have thus been proposed to decrease the cost while guaranteeing the electrochemical performance.^{116,117} In addition, the combination of alkaline and PEM technologies can also improve the electrochemical performance. For example, integrated systems that combine an anion exchange membrane with platinum-group-metal/low-cost transition-metal catalysts have been reported to show higher efficiencies when compared with the single alkaline and PEM electrolyzer.¹¹⁸

SOEC Electrolyzer. SOEC employing a solid oxide electrolyte traditionally works under high temperature and high pressure.¹¹⁹ Doped zirconia (YSZ) is the most commonly used material for solid oxide electrolytes. The planar SOEC cell configuration is favored owing to its easier manufacturability and better electrochemical properties when compared to tubular cells. The minimum electrical energy for the endothermic water electrolysis can decrease by 25% from 25 to 1000 °C.¹²⁰ Compared to the conventional low temperature alkaline and PEM electrolyzers, SOEC consumes less electrical energy and demonstrates lower electrode overpotentials, higher efficiencies, and faster reaction rates.¹²¹ However, the high temperature operation may reduce the mechanical stability of the electrode. To improve the robustness of the electrode under high temperatures, proton-conducting oxides may provide potential alternatives to conventional oxygen-ion electrolytes.¹²²

Other Water Splitting Technologies. Several studies of other water splitting technologies have been reported including thermochemical,¹²³ photoelectrochemical,¹²⁴ photocatalytic,¹²⁵

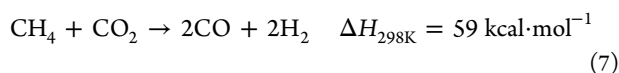
and even photobiological.¹²⁶ The principle behind the photoelectrochemical technique is similar to the electrochemical technique, except the required energy is provided directly by sunlight. The photoelectrodes are made of semiconductor materials to capture visible light. For photocatalytic water splitting, the powder catalysts are dispersed in water for evolving oxygen and hydrogen. Without the temperature swing, the thermochemical technique can reach a high efficiency for water splitting. There are, however, various obstacles that still need to be overcome, and as a result most of these technologies are far from mature and are likely to require significant laboratory studies prior to achieving industrial acceptance.

Challenge. The power consumption at 100% theoretical efficiency is 39.4 kWh/kg of H₂.¹²⁷ The levelized cost of hydrogen (levelized cost = net cost to install a hydrogen plant divided by its expected lifetime hydrogen output) from water electrolysis is around 4.5 US\$/kg, which is about 3–4 times more expensive than that from natural gas reforming (1.32 US\$/kg).¹²⁸ In the future, the energy promoting the water splitting should come from renewable sources because the energy derived from conventional fossil fuels will inevitably add to the total CO₂ emissions. Table 6 lists the operating conditions, efficiency, as well as the advantages/disadvantages of solar energy driven water splitting routes.¹²⁰

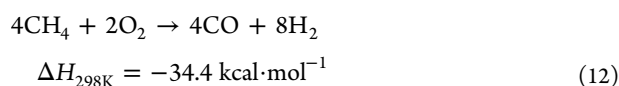
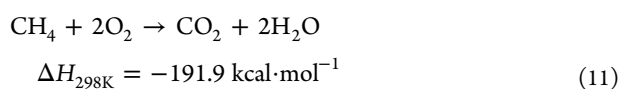
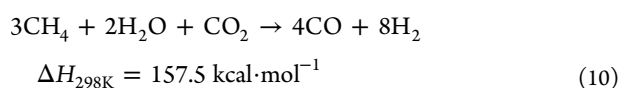
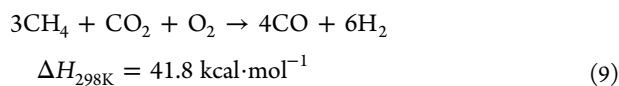
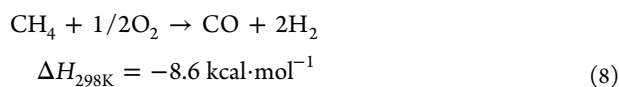
Current electrolyzers, including commercial devices, are very expensive. The following research directions should enable quantitatively lowering the production costs and aiding the implementation of renewable-energy-based H₂ production technologies for CO₂ conversion on a large scale.

- Employ photovoltaics (PVs), such as perovskites PVs in combination with electrolyzers to achieve higher renewable energy conversion efficiency and productivity.
- Improve the solar-to-hydrogen conversion efficiency and the life span of the electrolyzer taking into account the net energy performance, scalability, durability, activity, and long-term stability of electrodes.
- Find nontoxic and cheap materials for constructing the semiconductor photoelectrodes.
- Design sustainable manufacturing solar cells.
- Employ renewable energy driven electrolyzers with intermittent operation.
- Design reliable devices and smart electrolyzer-based H₂ production plants.

3.1.2. Dry Reforming. The recent advent of unconventional natural gas availability makes the dry reforming option as given by eq 7 very attractive for syngas production at relative low cost.¹²⁹



Single Dry Reforming. Dry reforming is a highly endothermic reaction. It traditionally requires elevated operating temperatures of 800–1000 °C to achieve high equilibrium conversion and to suppress the thermodynamic driving force for carbon deposition. Furthermore, deactivation associated with dry reforming cannot be completely avoided due to the carbon deposition. Although noble metals such as Ru, Rh, Pd, Pt, and Ir demonstrate high activity and excellent resistance to carbon deposition,¹³⁰ they are less practical than non-noble metals due to the limited availability and high cost. Various Ni-based catalysts with different supports and promoters have been widely studied. For example, silica supported Ni catalysts display a specific activity in dry reforming at 773 K within the range of 1.6–7.3 nm.¹³¹ Promoting Ni catalysts with noble metals may promote the catalytic activities and suppress the carbon deposition.¹³² At present, catalysts for dry reforming are still being evaluated at the laboratory level. In-depth studies of structure/support/promoter-performance, temperature/pressure-performance as well as reaction mechanisms would assist in guiding the modifications of existing catalysts and the discovery of new catalysts such as crystalline oxide catalysts and mesoporous catalysts.



Composite Reforming. Faced with the demand for economical large-scale implementations, modifications of existing dry reforming technologies or the exploration of novel reforming technologies need to concentrate on maximizing the carbon conversion rate while minimizing the required energy to reduce the total operating/capital cost as much as possible. Combining the endothermic dry reforming (eq 7, denoted as technology I) with the exothermic partial oxidation (eq 8) as bireforming (eq 9, denoted as technology II) may reduce the total energy required. The combination of dry reforming with steam reforming shown as eq 10 (denoted as technology III) can produce the appropriate H₂/CO ratio for methanol synthesis while avoiding any additional ratio adjustment steps.¹³³ Although a combination of CH₄ combustion (eq 11) with bireforming (eq 10), namely oxidative bireforming (eq 12) can achieve thermoneutrality,^{134,135} such oxidative bireforming is not very useful for CO₂ conversion

because the CO₂ required for bireforming is obtained completely from CH₄ combustion.

Cost and energy requirements must be carefully considered when selecting the optimal reforming technology from the three above-mentioned alternatives. Using methanol synthesis as an example, eq 10 illustrates that technology III can avoid the need for additional capital investment for adjusting the CO/H₂ ratio; however, the energy requirements of this approach would be much higher than technology I. Similarly, eq 11 indicates that technology II can reduce the energy requirements to a certain extent, but it does require a reliable source of O₂. The key question is whether an increase in capital investment (and associated depreciation costs) can be offset by the expected reductions in energy requirements. A detailed analysis would be needed for a range of process combinations and production scales.

Challenge. Dry reforming, bireforming composed of dry and steam reforming, and bireforming combining dry and partial oxidation reforming are three potential routes for converting CO₂ and CH₄ to syngas. As presented in Table 5, these three technologies have their distinct advantages/disadvantages and are not yet ready for practical deployment. From the viewpoint of large-scale industrial application, the following issues need to be further explored:

- Capital costs and energy requirements related to technology selection.
- Reaction mechanisms and catalyst surface/structure properties versus inhibition due to carbon deposition and catalyst deactivation.
- Durability enhancement via appropriate basic support/promoter.
- Long-term stability of catalyst via suitable operating mode selection.
- Innovative designs of novel reactors with enhanced mass/heat transfer properties.
- Overall large-scale heat/power integration including the reformer, external heat sources, and downstream processing units.

3.1.3. CO₂ Splitting to CO. Reducing CO₂ to CO followed by WGS is another route for synthesis gas production. The key idea behind this route is to develop a cost-effective and efficient CO₂ splitting system. When the electric-energy-based CO₂ reduction process is evaluated from a system-level perspective, energetic efficiency, Faradaic efficiency, conversion rate, long-term stability, and process economics are five important indicators that need to be considered for future commercialization of these technologies.

Electrochemical CO₂ Splitting. Similar to water electrolysis, in an electrolyzer, the cathode reduces the CO₂ whereas the anode is responsible for the oxygen evolution reaction.¹³⁶ CO₂ electrolyzers can achieve electron conversion efficiencies of higher than 50% at the cost of very high overpotentials (~1.5 V).¹³⁷ However, high overpotentials not only result in high electrical energy requirements but also represent inferior selectivity. A variety of approaches have been proposed for the identification and modification of electro-catalysts that could lead to electrochemical performance improvements in the reduction of CO₂ to CO.^{138,139} Transition metals, metal oxides, organometallic catalysts are the main candidates for CO₂ splitting. Among these candidates, Ag is the current state-of-the-art material, which has been extensively studied. In addition, various electrolytes as well as the operating conditions (pH values,

temperatures, and pressures) have also been systematically studied and evaluated.¹³⁶

Photodriven CO₂ Splitting. Photoelectrochemical, photocatalytic, and thermochemical technologies have also been investigated for CO₂ splitting to CO. The photoelectrochemical CO₂ reduction follows the same principle as photoelectrochemical water splitting. The required energy comes from deep UV light with wavelengths below 200 nm. Current research activities mainly focus on desirable photocathodes that enable the sufficient utilization of visible light irradiation.^{140,141} For photocatalytic technologies, the development of a highly efficient system focuses on electronically linking a suitable catalyst to a light capturing moiety.^{142,143} TiO₂ has been extensively evaluated and modified via composition and structure innovations owing to its superior long-term stability and durability.¹⁴⁴

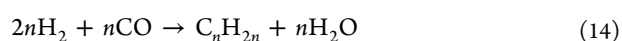
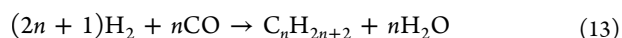
Thermochemical Cycle Technology. With temperatures of more than 2000 and 900 °C, respectively, one-step and two-step thermochemical cycles using metal oxide redox reactions may also be feasible pathways to obtain CO from CO₂.¹⁴⁵ Obviously, these high-temperature-based thermochemical routes are very energy and cost intensive, leading to potential additional CO₂ emissions. In addition, these thermochemical routes also require highly efficient materials that can withstand such very high temperatures for a considerable number of cycles.

Challenge. Compared to water splitting, CO₂ splitting is a more recent research area. As a result, large-scale deployment of CO₂ splitting catalysts and systems is unlikely to be seen in the near future due to several issues:

- The required energetic efficiency, Faradaic efficiency, and conversion rate of a specific material for electrochemical/photoelectrochemical technology have not been established.
- Better understanding is needed of the reaction mechanism, material properties as well as catalytic performance and operating conditions of photoelectrochemical/photocatalytic technologies.
- The solar energy conversion efficiency, selectivity, and conversion rate associated with the photocatalytic technologies are extremely low.
- The long-term stability and durability of the photocatalysts/electro-catalysts need to be evaluated for relatively large-scale devices.
- Sustainable process design of the CO₂ splitting system is needed.

3.2. Fischer–Tropsch Synthesis for Upgrading Syngas.

Fischer–Tropsch (F-T) synthesis is a commercial route for upgrading syngas to hydrocarbons. Generic reactions of F-T synthesis are given in eqs 13 and 14. F-T synthesis can be performed under either high or low temperature conditions. Following a polymerization mechanism, the products of F-T synthesis can be described by the Anderson–Schulz–Flory (ASF) distribution.¹⁴⁶ Light gas, olefins, liquid petroleum gas, naphtha, distillate, and wax are the main raw products of F-T synthesis. After downstream upgrading, C₂–C₅ olefins, aromatics, gasoline, kerosene, and diesel can be obtained.



Depending on the target products (fuels or chemicals), F-T synthesis commonly uses an iron-based catalyst or a cobalt-based catalyst where the addition of a promoter can raise the catalytic

activity and selectivity toward the target products.^{147,148} Low temperature F-T synthesis is prone to convert synthesis gas to diesel and wax, whereas high temperature F-T synthesis favors light olefins and gasoline production. On the basis of the specific catalyst and the operating conditions, F-T synthesis can also generate low olefins with high selectivity.¹⁴⁹ Selectivity and activity of a F-T catalyst are strongly dependent not only on its particle-size and activity-phase structure but also on the underlying support material. Novel characterizations, experimental investigations, and advanced computational approaches have been integrated with the aim of fundamental understanding of the composition/structure–performance relationships.¹⁵⁰ Furthermore, long-term stability¹⁵¹ and carbon deposition mechanism¹⁵² have also been given attention. In addition to catalyst innovations, the reaction medium such as in supercritical F-T synthesis can play a significant role in promoting the production of the targeted products.¹⁵³

Although a large number of catalysts have been claimed on laboratory level to be capable of maximizing the product yields, the number of commercially ready catalysts is limited. F-T synthesis will continue to evolve with advances in the development of next-generation catalytic materials for expanding the product portfolio and with innovative reaction systems for cost-effective implementation.

- Next generation F-T catalysts should enable controllable selectivity and long-term stability.
- Next generation F-T catalysts should have superior ability to inhibit greenhouse gas production including CO₂ and CH₄ as well as suppress carbon deposition.
- Next generation F-T synthesis technologies should be able to produce cost-effectively premium lubricant base stocks, high quality gasoline with high octane rating, and diesel with low cloud point.
- Next generation reaction systems for F-T synthesis should be capable of promoting mass/energy transfer and rapid heat removal via short-time contact with reactors in series, large amounts of recycle, and novel reactor structures.

3.3. Methanol/DME as an Intermediate. In addition to F-T synthesis, syngas can be converted to methane, methanol, higher alcohols, and other chemicals that could also be produced by direct hydrogenation of CO₂. Although the importance of hydrogenation of CO₂ to CH₄ has been emphasized in several reviews and perspectives,^{106,110} the current low natural gas (CH₄) price and the high capital/operating cost of the methanation process prohibits the thermodynamically favorable hydrogenation of CO₂ from being implemented economically on a large scale. Using an optimistic estimation, where the selectivity and conversion rate of the methanation catalyst is assumed as 100% and 50% and the renewable H₂ production cost is assumed as 2 US\$/kg of H₂, producing 1 kg of methane will cost at least 2 US\$ for the required H₂. Clearly, producing high-volume-low-value liquid fuels and high-value-low-volume chemicals from the hydrogenation of CO₂ may offer more economical benefit. Nevertheless, no matter which production route will be adopted, two simple principles should be kept in mind when deciding on the products and designing the process for CO₂ conversion: using more energy to produce a lower energy content material makes no sense; and the CO₂ emissions from the entire conversion process must be less than the amount of converted CO₂.

3.3.1. Methanol Production from Syngas. Methanol synthesis is a strong exothermic process. Gas-phase and liquid-phase operation are the two main routes for methanol synthesis from

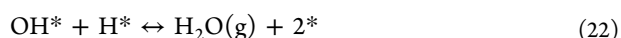
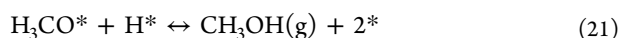
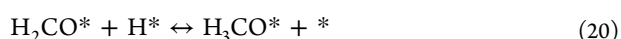
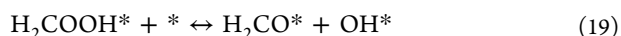
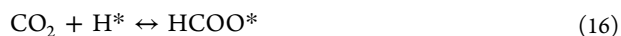
syngas. Compared with gas-phase methanol synthesis, liquid-phase synthesis exhibits more effective heat removal at the cost of a lower conversion rate. The byproducts from methanol synthesis contain DME and higher alcohols. Cu/ZnO/Al₂O₃ is the widely used industrial catalyst for producing methanol from gaseous mixtures (H₂/CO/CO₂) at elevated temperatures (200–300 °C) and high pressures (50–100 bar). Interactions between the active metals and the oxide supports are highly synergistic, and sensitive to the reactive environment.¹⁵⁴ Fundamental studies of Cu/ZnO/Al₂O₃ related to the nature of active sites, structure–performance relationships, and the role of each component has been extensively reported.¹⁵⁵ By simultaneously considering the individual properties of metal nanoparticles and the bulk properties of the catalysts, it is possible to establish the comprehensive knowledge needed for rational catalyst design that could enable precisely control of the activity, selectivity, and stability.

Even with the highly active catalysts that are available today, the actual commercialized methanol synthesis process is operated under a partial syngas conversion in each reaction stage to prevent overheating. Such operation leads to large recycles of unreacted syngas, which means extra capital cost for the compression system. Therefore, further studies should be undertaken to improve considerably the economic performance of potential large-scale methanol synthesis plants.

- Understand the reaction mechanism of methanol synthesis and the nature of the active site on Cu/ZnO/Al₂O₃, which dictates the methanol selectivity and productivity.
- For novel supported catalysts, the nanoparticle distribution–stability/durability relationships should be evaluated under industrially relevant conditions.
- Smart and sustainable heat management and process flowsheet design.

3.3.2. Direct Hydrogenation of CO₂. The direct CO₂ hydrogenation through a heterogeneously catalyzed sustainable process has gained significant momentum in recent years. It should be emphasized that direct CO₂ hydrogenation is not simply a case for re-engineering the current optimized syngas-based methanol synthesis technology. Two challenges including the reaction mechanism and selectivity toward methanol are linked to the direct methanol synthesis from CO₂ and H₂.

Reaction Mechanism. A number of contributions have focused on understanding the reaction pathway for methanol synthesis over supported Cu catalysts. The mechanism for direct methanol synthesis from CO-free CO₂ appears to be very similar to that of traditional methanol synthesis. The most likely reaction mechanism has been reported as follows (* denotes an adsorber species or a surface site):^{156,157}



Heterogeneous Catalyst Innovation. The key issue associated with heterogeneous catalyst development is how to inhibit RWGS as it produces CO, which directly reduces the methanol yield. Most catalysts used in the direct synthesis route have been modified from syngas-based methanol synthesis.¹⁵⁸ For example, an enhancement in the electron density of ZnO by encapsulating CdSe into the ZnO rod as core–shell structure can improve the selectivity toward methanol.¹⁵⁹ Cu/ZnO/ZrO₂ exhibits superior catalytic performance than Cu/ZnO/Al₂O₃ because ZrO₂ can better control catalyst texture and metal surface exposure.¹⁶⁰ Through the combination of experimental and computational studies, a novel Ni₃Ga₃ catalyst recently has been discovered for direct CO₂ hydrogenation to methanol with high activity and selectivity.¹⁶¹ Although its durability and stability are still unknown, the above Ni–Ga catalyst illustrates the potential of seeking novel catalysts for direct methanol synthesis that can give high methanol yield under low-pressure conditions.

Homogeneous Catalyst Innovation. Homogeneous catalysts also demonstrate potential for CO₂ hydrogenation.^{162,163} Apart from cascade reactions with different homogeneous catalysts, the hydrogenation of CO₂ to methanol can be achieved by using a single homogeneous ruthenium–phosphine catalyst under relatively mild reaction conditions.¹⁶² Metal-free systems such as phosphine–borane organo-catalyst also illustrate the potential for hydrogenating CO₂ to methanol.¹⁶³

The challenges involved in using homogeneous catalysts from an engineering perspective can be illustrated through the use of a type of (PNP) Ru^{II} catalyst for the homogeneous hydrogenation of ethylene carbonates for producing methanol and ethylene glycol.¹⁶⁴ As shown in Figure 7, even if the ethylene oxide can be produced from cheap shale-gas-derived ethane, such a system may suffer from expensive operating and capital costs because this two-stage homogeneous catalytic system calls for rather complex reaction-separation procedures. Additionally, the environmental performance/impact associated with this process should also be questioned.

Challenge. Although homogeneous catalysts for direct methanol synthesis can provide high activity and selectivity under mild operating conditions, it would appear that homogeneous catalytic systems cannot be implemented on a large scale in the near future due to the following four serious drawbacks:

- Low productivity.
- Poor long-term thermal stability and durability.
- Complex and expensive separation system.
- Difficult and cost-intensive catalyst recovery.

Compared with their counterparts for promoting the methanol synthesis from H₂/CO/CO₂ mixtures, heterogeneous catalysts for CO-free CO₂-derived methanol synthesis demonstrate important disadvantages. Large-scale implementation of these heterogeneous catalysts, require significant efforts particularly as it relates to the following issues:

- Low productivity.
- Slow kinetic rate.
- Low selectivity.
- Limited understanding of reaction mechanism.
- Unclear roles of support oxides on the catalytic reactions.

3.3.3. Electrochemical Routes for Methanol Production. Methanol produced via the electrocatalytic route is composed of a reduction at the cathode and an oxidation reaction at the anode. Using different reaction media and electrode materials, a variety

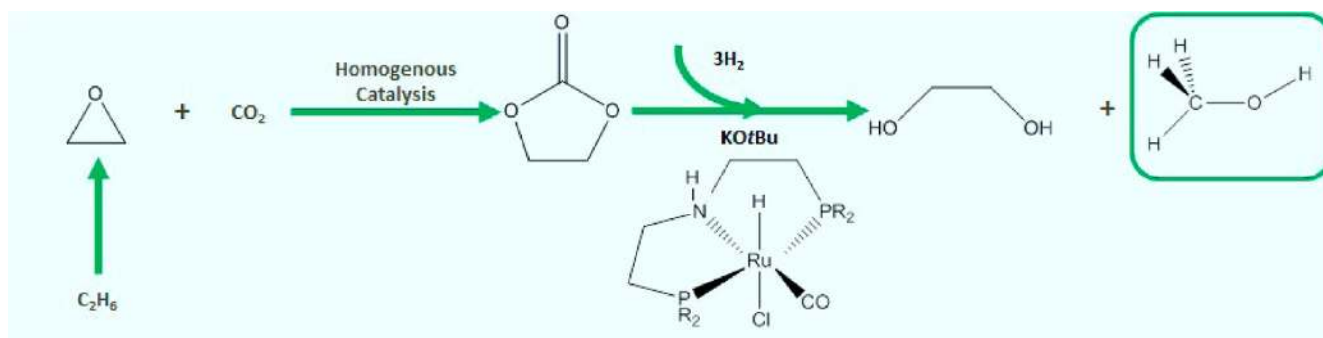
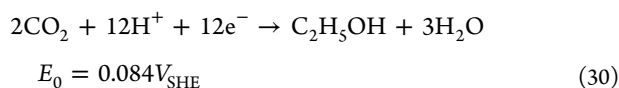
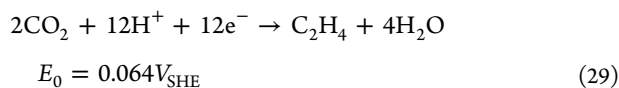
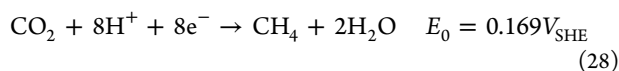
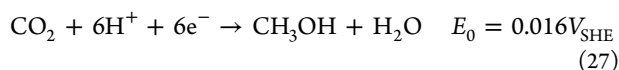
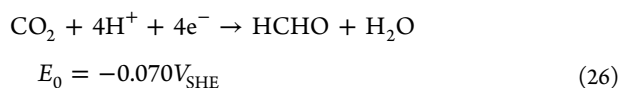
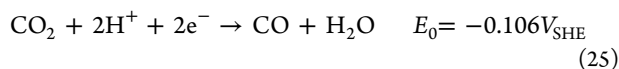
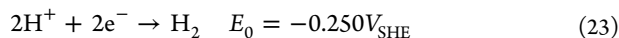


Figure 7. Chemical routes for hydrogenating CO₂ to methanol and ethylene glycol.

of additional products such as HCOOH and CH₄ can also be generated through various reduction pathways in gaseous and nonaqueous phases. Catalyst design, electrolyte selection, and electrode structure are three main aspects for effective electrochemical conversion of CO₂ to methanol.

Reduction Pathway. Equations 23–30 give detailed information about electron transfers associated with the main products. A more positive reduction potential indicates that the reaction is more thermodynamically favorable. Apparently, the CO₂ reduction toward HCOOH and CH₂O are thermodynamically less favorable than the hydrocarbon productions.^{165,166}



Electrochemical Catalysts. So far, metals, metal oxides, metal alloys, metal complexes, MOFs, polymers/clusters, enzymes, and organic molecules have been utilized as catalysts.^{167,168} Cu, Mo, and Ru are among the most promising electrodes for CO₂ electrochemical reduction to methanol. In general, heterogeneous electrochemical CO₂ reactions for methanol production feature lower densities and lower Faradaic efficiencies when compared with homogeneous reactions. Bifunctional catalysts composed of metals and organic catalysts can potentially show superior efficiency and conversion rate. A recent comprehensive review has summarized and compared different catalysts and electrode structures.¹⁶⁹

Reaction Medium. The majority of current research efforts use the aqueous solution as reaction medium. However, several

obvious disadvantages arise in doing so. The aqueous solution can slow the reaction kinetics and enhance the overpotentials that may require additional electrical energy. Furthermore, the aqueous solution would lower the conversion rate and selectivity. Thus, the methanol purity the electrolyzer is very low. Solid polymer electrolytes¹⁷⁰ and ionic liquids¹⁷¹ are two potential alternatives that can render/provide efficient mass transport and high productivity. It should be mentioned that, in addition to the aforementioned three key points, operating conditions, including pH, temperature, and pressure, also significantly affect the overall performance of the electrochemical conversion system.

Challenge. As a result of three serious challenging problems, none of the current electrochemical CO₂ conversion systems for methanol production are ready for industrial implementation.

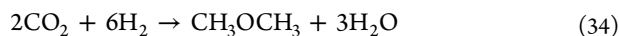
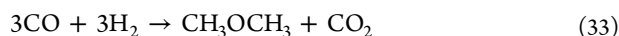
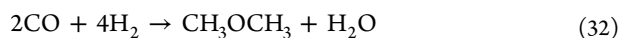
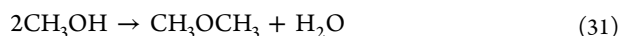
- Low energy efficiency, poor product selectivity, and unknown durability of the electrode are the most important reasons hindering the practical application.
- A cheap reaction medium that can provide high mass transfer rates and high productivity has not been found.
- Relationships between electrolyte composition and reaction performance as well as operating condition and reaction performance have not been figured comprehensively.

3.3.4. Photochemical Routes for Methanol Production. The photocatalytic conversion of CO₂ to methanol using high-energy-density sunlight is conceptually the ideal reaction. Research in this field focuses primarily on the development of novel nanostructured photocatalytic materials and the investigation of the reaction mechanism. Homogeneous and heterogeneous catalysts have been widely studied. Heterogeneous catalysts like TiO₂ can only utilize the ultraviolet portion of the solar spectrum, which is less than 40% of the total sunlight energy. In general, the required potential for CO₂ reduction is higher than the electron flat-band potential in the conduction band of TiO₂. Modifications of TiO₂ materials through tailored size and structure as well as composition can synergistically improve the efficiency.^{172,173} Recent developments mainly concentrate on new photocatalysts (e.g., novel oxynitrides of metals with d⁰ electronic structures, oxides of d¹⁰ metals, bimetallic nanoparticles, carbon nanotube, graphene, sulfide, or phosphide) and the corresponding novel configurations (e.g., core-shell structures, nanosheets, porous structures, hybrid nanostructures) offering large surface area, improved charge separation, and directional electron transfers.^{174–177} However, several unsolved questions continue to impede the scale-up of the above technologies.

- Current CO₂ conversion rates do not meet the requirements for scale-up.

- Corrosion-resistant and highly reproducible photocatalysts are needed.
- Mechanisms of light absorption, charge separation, and reaction pathway need to be better understood.

3.3.5. DME Production. Dimethyl ether (DME) is another important oxygenate that can be used as a clean-burning substitute for diesel. The relevant reactions are given by eqs 31–34. DME can be synthesized by the dehydration of methanol over an acid catalyst. As indicated by eqs 31 and 32, synthesis gas can also be used to synthesize directly DME under different reaction conditions and catalysts with specific byproducts.¹⁷⁸ As shown in eq 34, the third route for DME synthesis starts from CO₂/H₂ mixtures, where a multifunctional catalyst system combining methanol synthesis and dehydration is required.^{179,180} In the third route, half of the H₂ would be transferred to water. It would be best to recycle the water produced to electrolysis to improve the utilization efficiency of hydrogen. Compared with the CO₂-derived methanol synthesis process MegaMethanol, under similar conditions, the CO₂-derived DME synthesis process MegaDME shows lower productivities, but also lower byproduct contents.¹⁸¹ Furthermore, this DME synthesis process is ready for large-scale implementation and therefore provides a promising alternative for large-scale CO₂ conversion.



3.4. Oxygenates Valorization. Various commercial routes can be used to convert catalytically oxygenates (methanol/DME) to high-value-added products including olefins, aromatics, and transportation fuels. Several studies of oxygenate-to-hydrocarbon technology have been dedicated to catalyst innovation,¹⁸² reaction mechanism elucidation,¹⁸³ coke formation and deactivation suppression,¹⁸⁴ catalyst synthesis,¹⁸⁵ as well as reactor development and scale-up.¹⁸⁶

Light olefins including ethylene and propylene can be produced from the oxygenates-to-olefin (OTO) catalytic system with zeolite or SAPO molecular sieve as the catalyst. Acidity of the catalyst plays a vital role in olefin formation. The UOP OTO technology uses H-SAPO-34, and a fast fluidized bed reactor has been implemented successfully for producing mixtures of ethylene/propylene.¹⁸⁷ The Dalian Institute of Chemical Physics (DICP)'s MTO technology (DMTO) for producing ethylene/propylene utilizes a proprietary SAPO-34 type catalyst and a dense phase fluidized bed reactor.¹⁸⁸ The DMTO-II technology contains an additional C₄+ cracking fluidized bed reactor to improve the olefins yield. These two fluidized bed reactors share the same regenerator for catalyst regeneration as the MTO reaction and the C₄+ cracking uses the same catalyst. The selectivity toward ethylene and propylene of DMTO-II increases from 79.21% in DMTO to 85.68%.¹⁸⁸ Since 2010, nine DMTO/DMTO-II plants have come online with an olefins production capacity of more than 5.6Mt/y. Adjusting the Si/Al ratio of HZSM-5 or impregnation of promoters can improve the propylene selectivity and reduce coke formation. Lurgi zeolites ZSM-5-based MTP technology can produce propylene with very high selectivity under relatively high temperatures and low pressures.¹⁸⁹ Methanol-to-gasoline technologies have also been evaluated from the engineering¹⁹⁰ and theoretical viewpoints.¹⁹¹

The ExxonMobil methanol-to-gasoline (MTG) technology based on H-ZSM-5 and fixed bed reactor has commercially produced high quality gasoline from methanol or DME.¹⁹² The H-ZSM-5-based Topsøe Integrated Gasoline Synthesis (TIGAS) technology of Haldor Topsøe AS was demonstrated in pilot scale in the mid-1980s.¹⁹³

When examining the current deployment of the above-mentioned commercial technologies for oxygenate conversion around the world, especially for the coal-driven-based chemical industry in China, most of these projects focus on lower olefins production. Implementation of methanol to aromatics may further enhance the potential profit margin. Methanol-to-aromatics (MTA) technologies using ZSM-5 zeolite catalysts were first developed by Mobil technology; since then, several catalytic systems have been proposed. In general, aromatics production from syngas follows three main routes:

- Methanol to olefins followed by oligomerization.
- Methanol to gasoline followed by separation of aromatic components.
- Naphtha production from F-T synthesis followed by catalytic reforming.

However, these processes suffer from high capital costs for producing aromatics because of the multistage reaction and complex separation steps. An intensified one-step aromatics production from methanol is desirable. As generally demonstrated by Figure 8,¹⁹⁴ a fluidized-bed-based MTA (FMTA) plant can produce aromatic C₈ mixtures with high yield at the cost of complex separation requirements.

3.5. Higher Alcohols as Intermediates. Higher alcohols are another type of intermediates for CO₂ valorization. Although several electrochemical/photochemical CO₂ conversion routes for higher alcohols production have been proposed,^{195,196} they share similar disadvantages with the electrochemical/photochemical CO₂ conversion routes for H₂ and methanol production. This paper will only cover the catalytic and biochemical as two main routes for producing higher alcohols.

3.5.1. Catalytic Production of Higher Alcohols. Ethanol and higher alcohols have been regarded as promising fuels or additives which can be blended with gasoline to increase the octane number and to reduce emissions of NO_x and CO₂.

Reaction Mechanism. The production of ethanol and higher alcohols is thermodynamically favorable but kinetically limited. The overall stoichiometric reaction for alcohol synthesis is given by eq 35:



Several research works^{197,198} conclude that the linear alcohol products follow the Anderson–Schulz–Flory (ASF) distribution given by eq 36:

$$\log(w_n/n) = n \log \alpha + \log((1-\alpha)^2/\alpha) \quad (36)$$

where w_n is the weight percentage of C_n alcohol, n is the number of carbon atoms, and α is the probability of chain growth. To achieve high catalytic performance for producing ethanol and higher alcohols, noble Rh-based catalysts, modified methanol-synthesis-based catalysts, modified F-T synthesis Fe-based catalysts, and modified Mo-based catalysts have been investigated.^{199,200} Table 7 lists the operating conditions and advantages/disadvantages associated with these four types of catalysts.

Catalytic System. Although Rh-based catalysts are the most promising candidates, the associated prohibitive cost and limited

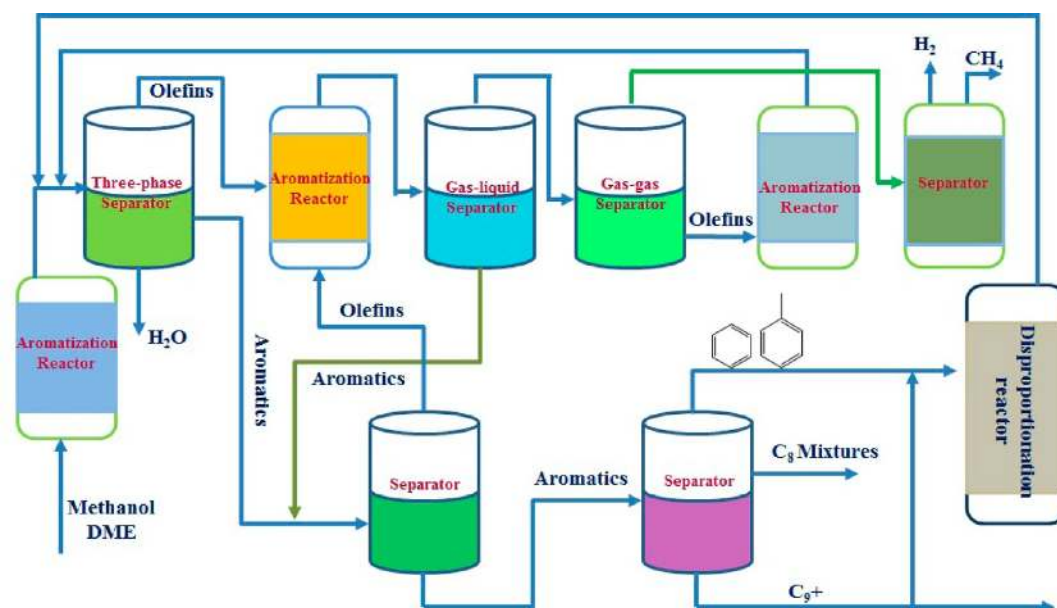


Figure 8. Schematic diagram of aromatics production from oxygenates based on fluidized bed reactor technologies with a recycle of byproducts for high carbon utilization.

Table 7. Comparisons of Four Types of Catalysts for Mixed Alcohol Synthesis

catalyst type		operating condition		advantage	disadvantage	
	major promoter	temperature (°C)	pressure (bar)			
Rh-based catalyst		300–320	~70	high selectivity; high conversion rate	expensive material	
modified methanol-based catalyst	Cu/ZnO	alkali	275–400	50–160	cheap materials	high methanol selectivity; very low mixed alcohol yield
	Cu/ZnO/Mn	alkali, Co, Cr ₂ O ₃	~400	100–180	moderate mixed alcohol yield	high methanol selectivity
	Cu/Mn	Ni, Fe, Co	280–340	60–130	cheap materials	very low mixed alcohol yield; very high methanol selectivity
modified F-T-based Fe catalyst		Cu, Zn, Pd, Ga	330–350	~80	reasonable activity; high CO conversion rate	low alcohol selectivity; poor long-term stability
modified Mo-based catalyst	sulfide oxide	alkali, Co	250–330	70–210	sulfur resistant; low sensitivity to CO ₂	low activity
			230–300	60–130		

supply prevent their practical implementation on a large scale. Earth-abundant and inexpensive metals are desirable candidates. Because the side reactions producing methanol and lower alkanes simultaneously occur, various approaches including modifying promoter, structure, and operating conditions (including feed composition, pressure, temperature, and space velocity), have been studied to improve the selectivity/activity and to suppress those undesired reactions.²⁰¹ Lower H₂/CO ratio favors higher selectivity but lower activity.²⁰² Modified MoS₂-based catalysts can demonstrate high selectivity and low coke deposition at the expense of low activity. Furthermore, MoS₂-based catalysts traditionally require high pressures to obtain reasonable productivity. Numerous supports, such as SiO₂, TiO₂, MgO, Al₂O₃, CeO₂, and carbon materials, have been studied to enhance higher alcohol selectivity and productivity by promoting high dispersion of MoS₂.²⁰³ It should be mentioned that, apart from the aforementioned catalyst modifications, feed composition adjustment, and operating condition changes, reaction medium can also affect the productivity of the higher alcohols. Recent work demonstrates that supercritical hexanes not only enhance the extraction of alcohol products from the

catalyst pores to promote the heat/mass transfer but also improve the selectivity and productivity of higher alcohols.²⁰⁴

Challenge. Studies of catalysts for higher alcohol synthesis have achieved significant improvements. However, to date, none of the above catalytic systems are commercially viable. The following aspects call for further research involving different disciplines:

- The effect of CO₂ on higher alcohol synthesis.
- Catalysts with desired properties under industrially relevant conditions.
- Scalable and cost-effective synthesis routes for catalyst manufacturing on large scale.
- Sustainable process design for separating mixed alcohols.
- Innovative reactor design promoting high mixed alcohol yield and CO conversion rate.
- Smart and sustainable process design for higher alcohol synthesis.

3.5.2. Biochemical Production of Higher Alcohols. Photosynthetic routes that directly generate products using the light/dark reactions and nonphotosynthetic routes that utilize a man-made device to gather power for driving the reaction are two

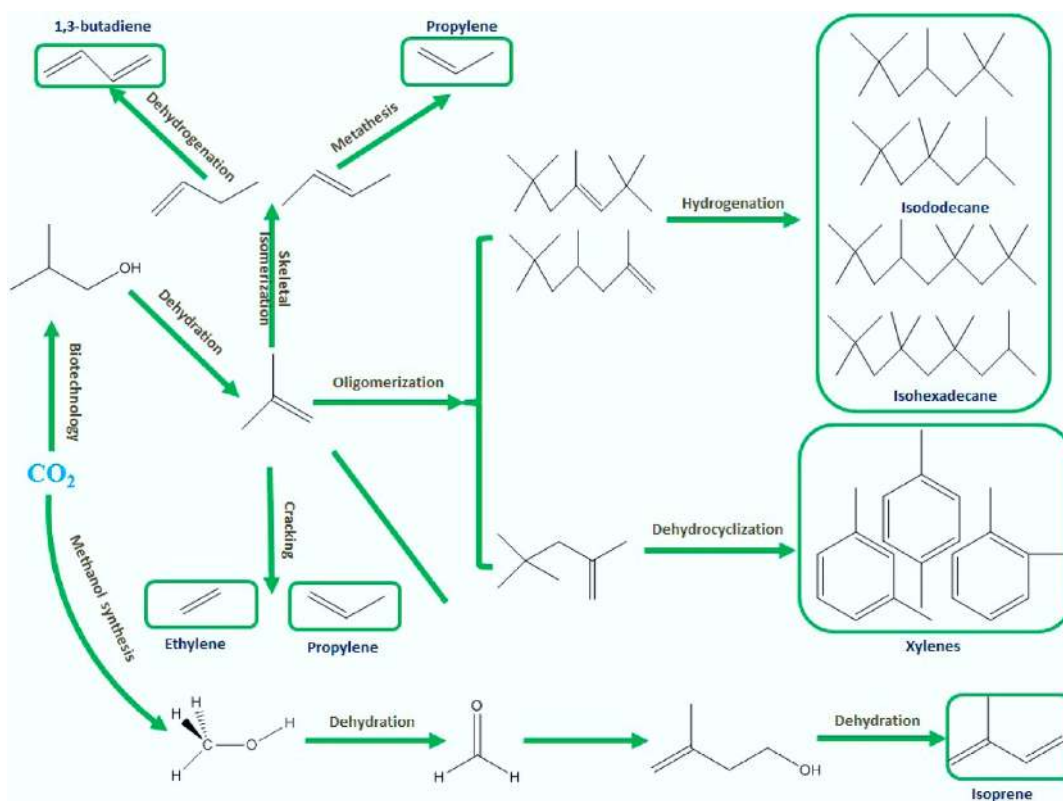


Figure 9. Selected examples of biochemical CO₂ conversion routes for producing olefins, aromatics, and jet fuel.

biological approaches for the production of value-added fuels and chemicals from CO₂.

Pure Biochemical Synthesis. Recent advances in synthetic biology and metabolic engineering are moving the non-photosynthetic approaches for biological fixation of CO₂ into liquid fuels and chemicals from concept to reality.²⁰⁵ Unlike catalytic conversion routes, biotechnologies for converting CO₂ to mixed alcohols can exhibit high selectivities toward target products at ambient conditions. Several attempts have been put forward to circumventing the overall low efficiency of photosynthesis in plant/algae through developing novel enzymes and engineered microorganisms. For example, cyanobacteria are suitable organisms that can be applied to produce fuels such as *n*-butanol and 2,3-butanediol directly from CO₂ without going through lipid synthesis.^{206,207} Higher alcohols and olefins can be effectively produced by *Synechococcus elongatus* PCC 7942 and *Synechocystis* PCC 6803 with specific synthetic pathways.²⁰⁸ Moreover, a recombinant cyanobacterium *Synechocystis* PCC 6803 can produce 720 mg of ethylene per liter each day, which is higher than those reported for microorganisms generating higher alcohols.²⁰⁹ Compared to traditional catalytic processes for producing alcohols, biological approaches can potentially avoid the release of large amounts of CO₂ if they can be successfully scaled up.

Hybrid Biological Synthesis. Combining electrochemical techniques and biological approaches, to some extent, can improve the utilization efficiency of electrical energy. A lithoautotrophic microorganism, *Ralstonia eutropha* H16, has been genetically engineered to produce isobutanol and 3-methyl-1-butanol in an electro-bioreactor.²¹⁰ CO₂ as the pure carbon source and electricity as the sole energy input are introduced to promote this electro-bioreactor. Although this combination is in its early stage with certain disadvantages, especially low

productivity, it still opens the possibility of the CO₂ bio-conversion to higher alcohols driven by electricity.

Derivates of Higher Alcohols. If these biochemical routes can be combined with commercial downstream chemical upgrading technologies, the energy utilization and environmental impacts can be ameliorated. Figure 9 gives an example of such a combination. The biological-derived higher alcohols can be subsequently converted to light olefins, aromatics, and liquid transportation fuels through traditional oligomerization and dehydrocyclization technologies.

Challenge. Several unresolved issues may prohibit the large-scale implementation of biological CO₂ conversion in the near future.

- Overall yield of the main product is very low, making downstream recovery and separation a challenging problem.
- Scalability of highly efficient laboratory-scale biological routes has not been evaluated.
- Robustness and durability of enzymes have not been systematically investigated. Indeed, biocatalyst-poisoning under realistic industrial conditions is one of the biggest challenges.
- Evaluation of the capital cost of bioreactor/separation systems and productivity of the engineered organism, both of which govern the economics of such biological processes, have not yet been performed.

3.6. CO₂ to Organic Chemicals. A wide range of electrochemical, photochemical, and biochemical routes have been explored to reduce CO₂ to organic chemicals with the aim of developing efficient energy storage.

Formic Acid. Formic acid production has been given the highest priority because it is a favorable energy and H₂ carrier.

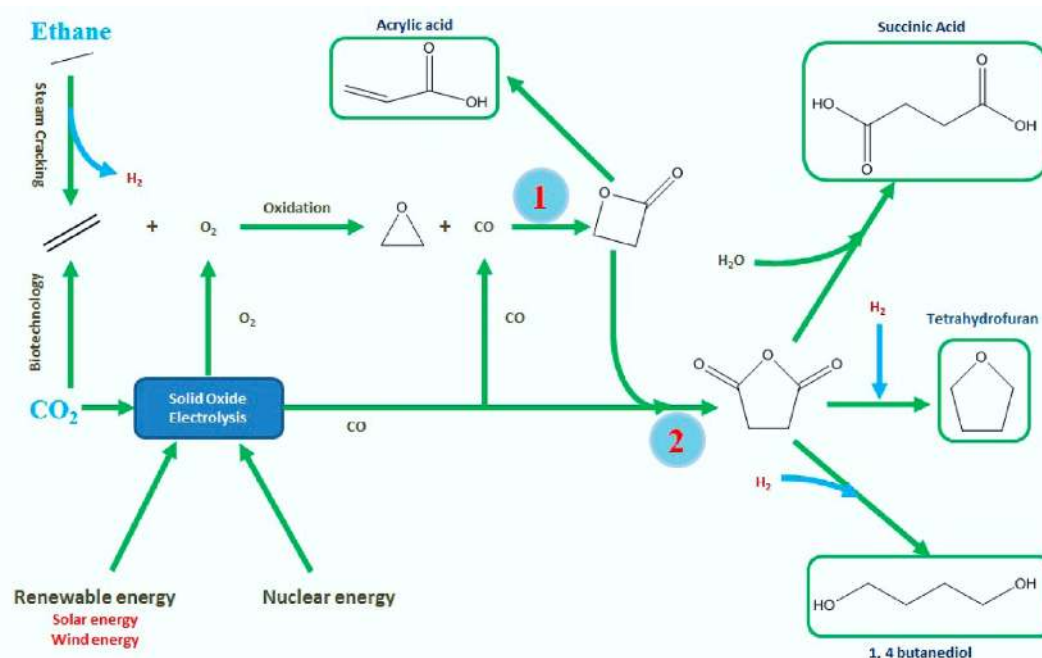


Figure 10. Potentially integrated conversion route for producing acrylic acid and 1,4 butanediol from CO₂.

Molecular catalysts such as iridium, ruthenium, and rhodium can enhance the conversion rate of CO₂ to formic acid at the cost of high temperatures and high pressures. A cobalt-based homogeneous catalyst, namely Co(dmpe)₂H (dmpe: 1,2-bis(dimethylphosphino)ethane), offers a higher conversion rate than that of rhodium-based alternatives at room temperature.²¹¹ Enzyme-based biotechnological routes can also efficiently hydrogenate CO₂ to produce formate.²¹² Novel photocatalysts such as MOFs and graphene–enzyme-based catalysts under visible light irradiation demonstrate outstanding reaction behavior.^{213,214} It should be noted that converting CO₂ to formic acid on a large scale will not be advisable because of its relatively small market and lower energy density compared to traditional liquid fuels.

Other Organic Chemicals. Other organic chemicals such as formaldehyde, acetaldehyde, acrylic acid, methyl formate, and 1,4 butanediol, which are traditionally produced from fossil fuels, can be manufactured from CO₂. For example, the production of formaldehyde can be accomplished from CO₂ and seawater under ambient conditions based on a boron-doped diamond electrode,²¹⁵ and seawater serves as the source for both electrons and protons. To tackle the low conversion rate and productivity associated with stand-alone biochemical, electrochemical, or photochemical routes, it is desirable to integrate these routes with traditional (thermo) chemical routes to offer high-quality target products with excellent selectivity and high raw materials utilization. For example, US Novomer has developed a process for producing acrylic acid taking advantage of the North American shale gas boom.²¹⁶ This “drop-in” production process is expected to reach pilot scale of 2000 tonnes/year by 2015. As depicted in Figure 10, the required CO comes from a solid oxide electrolyzer that can use renewable energy or nuclear energy, whereas the required ethylene can be produced from CO₂ following biotechnology conversion routes or from steam cracking of ethane. If the Intellectual Property associated with the specific catalysts (shown as red numbers in the figure) can be shared by Novomer, the possibility and economic performance of

a polygeneration facilitate, including other higher-order chemicals such as 1,4 butanediol, can be systematically evaluated.

Challenge. Because of the issues listed below, conversion of CO₂ toward organic chemicals is not yet a viable route for large-scale implementation.

- Limited market requirements.
- Poor yield of the organic chemical and low conversion rate of CO₂.
- Simple and efficient catalyst recycle as well as economically feasible separation associated with homogeneous catalytic processes.

3.7. Industrial Activities for CO₂ Conversion. In addition to various academic studies, industry has also been extensively involved in the development of efficient CO₂ conversion processes. Carbon Recycling International (CRI) in Iceland has launched the first plant to produce methanol from a geothermal waste stream with a capacity of 4000 tonnes per year.²¹⁷ Mitsubishi’s Carbon Dioxide Recovery (CDR) plant has been constructed for the Qatar Fuel Additives Company (QAFAC).²¹⁸ This QAFAC plant captures 500 tonnes per day of CO₂ from its methanol reformer stack based on Mitsubishi’s proprietary KS-1 solvent. The captured CO₂ will produce a total of 982 350 tonnes per year of methanol that will be converted to 610 000 tonnes per year of MTBE. Recently, CRI and Mitsubishi Hitachi Power System Europe (MHPSE) formed a strategic alliance to deliver a power-to-methanol solution, which uses CO₂ from flue gas and H₂ from wind/solar driven water splitting, to enhance the efficiency of coal and chemical plants.²¹⁹ Table 8 gives a partial list of other industrial activities. It can be seen that almost half of these projects are focused on producing liquid fuels and high-value added chemicals via biochemical or photochemical routes. The productivity, conversion rate per pass, durability, and stability associated with biochemical/photochemical techniques still need to be improved.

It is very important to emphasize that capital cost and conversion efficiency are two issues affecting the sustainable

Table 8. Partial List of Studies of CO₂ Conversion in Industry

company	route	product
Novomer	thermochemical	propiolactone/acrylic acid/butanediol
Liquid Light	electrochemical	ethylene glycol
Newlight	biochemical	plastic
Skyonic	biochemical	hydrochloric acid
Dioxide Materials	electrochemical	gasoline/diesel/chemicals
LanzaTech	biochemical	liquid fuels/plastics
Bayer Technology	zinc-based catalyst	polyurethane plastic
Brain	microorganism	fine and specialized chemicals
Joule	biochemical	diesel/jet fuel
Geely Group/CRI	thermochemical	methanol
Audi/Global Bioenergies	biochemical	bioisooctane
Audi/Joule	biochemical	ethanol/diesel
Audi/Sunfire	thermochemical	diesel
Krajete GmbH	microorganism	methane
Panasonic	photochemical	formic acid
Greenearth	solar dissociation	syngas
Solar Fuel	thermochemical	syngas
Sunfire GmbH	thermochemical	diesel/kerosene
Proterro	biochemical	sugars
Elcriton	microbial catalyst	biofuel
Renewable Energy Institute International	thermochemical	liquid fuels

development and deployment of promising CO₂ conversion routes on a large scale.

3.8. Conclusions on CO₂ Conversion. Because of the very low efficiency and productivity, single-step electrochemical and photochemical CO₂ conversion technologies are unlikely to be deployed in the near/medium future. Instead, the rapid progress in technologies for renewable electricity production, especially the achievements in wind energy and perovskites photovoltaic cells, will be capable of deploying a combination of electricity-/solar-driven H₂ production in the near/medium future. Direct hydrogenation of CO₂ to methanol has been industrially implemented; however, they cannot be economically deployed on a large scale in the near future. Table 9 lists the advantages and disadvantages for various CO₂ conversion routes.

If renewable-energy-based water splitting and gas-phase heterogeneous catalysts for dry reforming become more reliable,

this combined process could be seamlessly interfaced with existing commercial syngas/oxygenates upgrading plants for producing value-added products as illustrated in Figure 11. In other words, compared with the photochemical/electrochemical/biochemical CO₂ routes, catalytic and thermochemical conversion of CO₂ are more promising for large-scale deployment in the near/medium future. When designing a large-scale CO₂ conversion process, the performance of traditional refineries and biomass/natural-gas-based (bio)refineries must be considered to ensure the large-scale CO₂ conversion process is competitive.

4. COMPUTATIONAL METHODS AND TOOLS FOR THE CO₂ VALUE CHAIN

In parallel to experimental studies, fundamental molecular-modeling-based computational approaches can provide a wide range of microscopic information not only for visualizing the property/functionality associated with materials for CO₂ capture and conversion but also for elucidating CO₂ adsorption, absorption, transportation, and reaction mechanisms. Engineering-level device properties for CO₂ capture and conversion, along with system economics and ecological performance can be obtained from macroscopic level computational models. In this section, a brief overview of a selection of these computational techniques is given.

4.1. Computational Approach for Materials Development. Computational approaches can aid in the selection of optimal materials for the CO₂ value chain by screening a large set of candidates where experimental screening may be cost/time-consuming or even impractical. Another role of computational approaches is to discover novel materials. Grand Canonical Monte Carlo (GCMC), Molecular Dynamics (MD), and Density Functional Theory (DFT) have been extensively adopted to calculate the material properties such as activity, isotherm, heat of adsorption, selectivity, permeability, and surface characteristic.^{220,221}

4.1.1. Specific Material Simulation. Realistic CO₂ capture/valorization processes typically operate under extreme conditions of elevated temperatures (syngas cleaning up, mixed alcohol synthesis), pressure gradients (natural gas sweetening, methanol synthesis), and high volumetric flow-rates of complex gas mixtures (postcombustion capture, large-scale methanol synthesis). Unfortunately, it is sometimes difficult or impossible to determine experimentally high-resolution condition–function

Table 9. Summary of Advantages/Drawbacks of CO₂ Conversion Routes

	technology	main product	advantage	disadvantage
CO ₂ splitting	electrochemical route	CO	utilize renewable sources	High capital cost
	photochemical route	CO	CO/O ₂ produced separately; utilize solar energy	low energy efficiency
	thermochemical cycle	CO	high efficiency CO/O ₂ produced separately	complex system design; harsh operation conditions
	dry reforming	syngas	take the advantage of cheap CH ₄	energy intensive; expensive catalyst cost
CO ₂ conversion	thermochemical	FT liquids/olefins	viable routes	low selectivity to main products; unclear CO ₂ –FT reaction mechanism
	thermochemical	methanol	commercially available	slow kinetics; low productivity; harsh conditions for heterogeneous catalyst; challenge to scale-up homogeneous catalyst
	electrochemical route	methanol	utilize renewable sources	unknown durability; low energy efficiency; mass transfer limitations; unfavorable product selectivity
	photochemical route	methanol	utilize solar energy	low productivity; low conversion rate; mass transfer limitations; low photon efficiency of materials
	biochemical route	mixed alcohols	ambient operation conditions; favorable selectivity to products	difficulty to scale up; unknown long-term durability; challenge to downstream separation

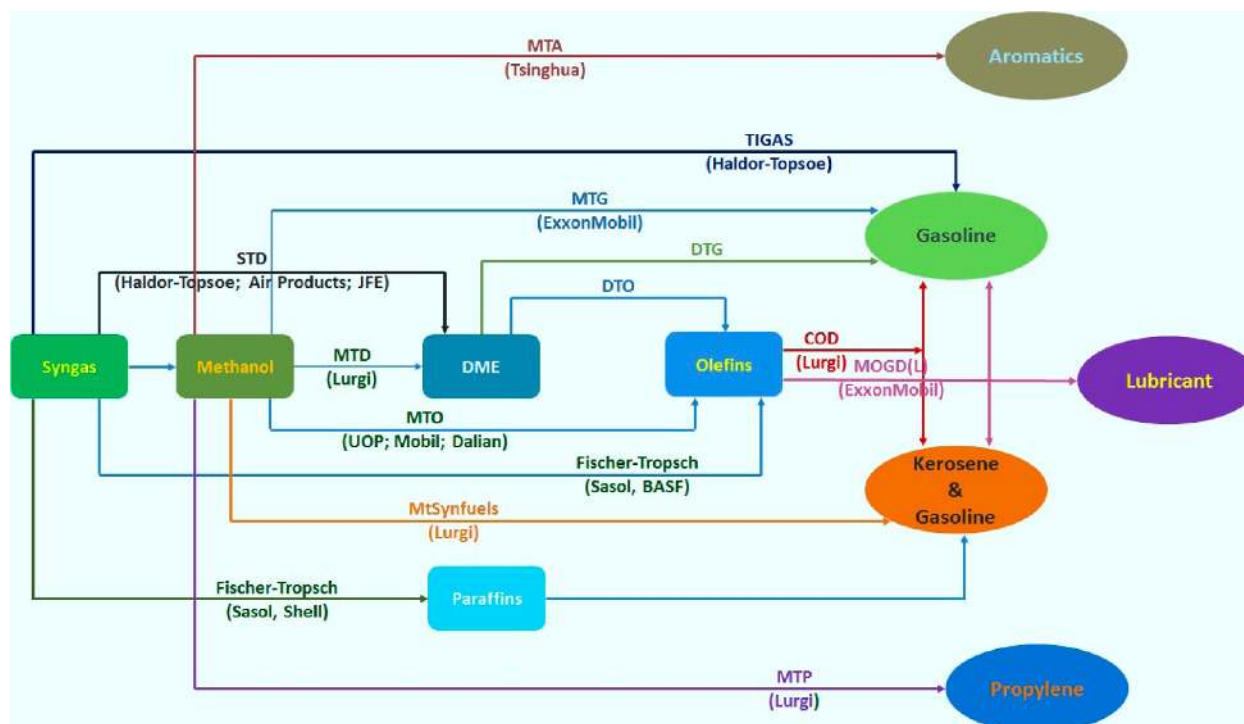


Figure 11. Commercial conversion routes for manufacturing value-added products from syngas.

relationships of materials under these harsh conditions. In such context, computational approaches can predict capture/catalytic characteristics based on appropriate molecular models and thus provide a valuable complement to experiments for improving insights into the materials' performance over a wide range of operating conditions.

Applications in CO₂ Capture. The operating condition–performance relationship and the property–performance relationship are two main reasons for simulating a specific material for CO₂ capture. Gas–gas and gas–host relationships explored by force fields have been widely used to compute the thermodynamics and transport properties under given operating conditions via MD or Monte Carlo. These simulations have been demonstrated as effective approaches for predicting the properties of materials, such as the adsorption and diffusion properties of zeolites/MOFs^{222,223} and CO₂ selectivity of porous coordination networks.²²⁴

Traditional experimental methods for tailoring materials with different compositions, topologies, loadings, surface areas, and sizes follow a trial-and-error approach. Indeed, these tedious experimental synthesis and evaluation/studies can also be simplified by computational approaches. In the past few decades, property–performance relationships and understanding of the microscopic mechanisms of several vital materials have been computationally elucidated.^{225,226} For example, CO₂ adsorption of Mg-MOF-74 has been extensively computed based on traditional and enhanced force field.²²⁷

Applications in CO₂ Conversion. Efficient atomic-level models can describe the nature of active sites, role of promoters, and support effects. Through computational prediction of the structure–activity and composition–activity relationships, molecular-level models can guide the rational design of new homogeneous and heterogeneous catalysts for CO₂ conversion.

Computational DFT-based techniques show promise to elucidate the role of additional elemental compositions on

conventional Al₂O₃ supported heterogeneous catalysts for CO₂ hydrogenation to methanol.²²⁸ Combined with in situ surface characterization techniques, DFT calculations have also been extensively applied for evaluating the compositions and structures of bimetallic alloy, metal semiconductor, oxide nanoparticles, and core–shell nanoparticles for photocatalytic CO₂ reduction.²²⁹ Additionally, hybrid DFT-based first-principle calculations have been carried out to compute the theoretical photovoltaic conversion efficiencies of CH₃NH₃PbI₃ perovskites, ZnSnP₂, CdSnP₂, and Zn_{1-x}Cd_xSnP₂ alloys for different structure and compositions,^{230,231} and to analyze the intrinsic defects of Cs₂SnI₆ perovskites.²³² Apart from the elucidation of the catalyst characteristics, the reaction mechanisms of the CO₂ conversion process can also be studied by atomic- and molecular-level models. For example, combined DFT techniques with microkinetic models have been used to study the reaction pathways for CO₂ and CO hydrogenation to methanol and the subsequent methanol to hydrocarbons.²³³

Challenge. The computational approaches can be faster than their experimental counterparts. However, these computational results depend heavily on the efficiency and accuracy of the model used.²³⁴ The assumed parameters for pure computational activities sometimes may be physically unrealistic. For accelerated development and deployment of reliable materials for the CO₂ value chain, a combination of computational approaches and experimental efforts is needed to obtain desirable materials with reliable and robust properties. Two challenges should be given particular attention:

- Can we get sufficient experimental data as experimental and computational researchers are currently working separately?
- Can the obtained data guarantee accurate predictions with the resulting models?

4.1.2. High-Throughput Computational Screening. Materials investigated for the CO₂ value chain to date only account for a tiny fraction of the possible candidates. Especially, given the large

number of potential topologies, linkers, and metal centers, there is an almost unlimited number of MOFs that could be investigated. Experimental screening of all these conceivable materials is limited by high costs and time-consuming procedures of synthesis. Thus, this experimentally intractable question has promoted high-throughput materials screening, which can narrow down the immense number of alternatives, as a very active area of research.

Descriptor Setup. The first issue for a computational-based screening approach is the criteria setup. Once a physically and chemically meaningful descriptor is accepted, the screening and ranking for all material candidates within the repository can be achieved intrinsically or extrinsically. In addition to existing descriptors such as selectivity, permeability, and capacity, several new indicators have been proposed.²³⁵ For instance, a new indicator called parasitic energy has been proposed for ranking hundreds of thousands of zeolites and ZIFs for CO₂ capture.²³⁶ More recently, almost all the synthesized covalent organic frameworks (COFs) to date have been screened based on the differences in the adsorbability of adsorbates.²³⁷

It should be mentioned that utilization of a single indicator for screening materials may lead to suboptimal candidates. For example, only considering the uptake of porous material for CO₂ capture may lead to difficulties in regeneration. Composite indicators rather than a single one should be used to screen the candidates. Two interesting examples discussed here are the discovery of desirable photovoltaic solar cells and photo-electrochemical cells, respectively. On the basis of the introduction of a composite descriptor composed of spectroscopic limited maximum efficiency (SLME), bandgap, shape of absorption spectra, and material-dependent nonradiative recombination losses, the top materials including CuInSe₂, CuGaSe₂, and CuInS₂ were identified from an inorganic crystal structure database with 150 000 candidates via in silico screening.²³⁸ Top oxide and oxynitride candidates for photo-electrochemical cells for water photosplitting were identified from a vast space of 5400–19 000 different oxides, oxynitrides, oxyfluorides, and oxyfluoronitrides with different structures via chemical/structural stability under irradiation, size, and position of the bandgap-based screening.^{239,240}

Computational Algorithm and Platform. The screening of existing or hypothetical microporous solid materials and membranes traditionally calls for expensive MD simulations for computing adsorption properties and diffusion coefficients.²⁴¹ Therefore, high-throughput computation is the second issue for large-scale computational screening approaches.²⁴² From the perspective of computing and systems engineering, fast computational models/algorithms and support platforms are required. A recent approach integrating transition state theory with a graphic processing unit (GPU),²⁴³ which benchmarked over 87 000 zeolites, provides an excellent starting point for the development of high-throughput computational approaches. In addition to innovative computation platforms, advanced screening algorithms such as stochastic programming and machine learning are also expected to be capable of accelerating the large-scale screening of large numbers of material candidates for the CO₂ value chain.²⁴⁴

Challenge. In silico high-throughput screening can significantly expedite and simplify the materials discovery procedure. However, it is still far from being a magic box for materials discovery for CO₂ capture and conversion. In general, three challenges still need extensive further research.

- Define the appropriate descriptors to avoid excessively large computation times.
- Develop efficient algorithms and platforms to reduce the computation burden of DFT/MD calculations.
- Define descriptors that can correctly represent/predict long-term durability and stability.
- Define generic descriptors that can effectively predict and capture a diverse set of properties of materials under various operating conditions.

4.1.3. Inverse Discovery of New Materials. Compared to the aforementioned screening approaches for searching candidates on the constrained compositional and structural search space, computer-aided inverse design as the reverse route of the conventional approach analysis is a new route (Figure 12). The



Figure 12. Computer aided inverse design of materials with predetermined functionality for the CO₂ value chain.

main idea behind computational discovery of new materials is that molecular fragments can be assembled to generate candidate structures meeting the desired property constraints, and these candidates are subsequently ranked using a set of performance criteria/properties.²⁴⁵ The ability to define chemical structures with predetermined functionality is key to finding new materials. In general, approaches for computer aided material discovery can be categorized in two main groups: (1) Enumeration approaches including generation and evaluation, which is similar to the above-mentioned screening approaches, and (2) mathematical programming approaches. Mathematical programming approaches have been used to explore novel materials for CO₂ capture,²⁴⁶ whereas applications in CO₂ conversion are quite rare. However, recent advances in inverse design of chemical products such as solvents for separation in the (petro) chemical industry^{247,248} can be leveraged to promote the discovery of materials for CO₂ capture and conversion.

4.1.4. Summary. Computational material simulations can aid experimental research in evaluating material properties for various compositions and operating conditions. High-throughput materials screening and computer-aided molecular design (CAMD) are two approaches that can assist in the discovery of novel materials for CO₂ capture and conversion. The former approach defines structure–property relationships and then uses them to predict and rank the candidate materials. Whereas the computer-aided molecular design approach seeks desirable material structures meeting specific property targets. The identified optimal candidate materials should exhibit high potential to be synthesized before more thorough computational and experimental evaluations are undertaken. In conclusion, computational material discovery, especially inverse design, represents a largely unexplored and exciting opportunity to identify novel materials for the CO₂ value chain. Bridging the gap between these theoretical predictions and experimental synthesis requires close collaboration across different disciplines. Two big challenges associated with these discovery routes are

- Developing a realistic synthesis pathway for such novel materials with specific structure and desired building blocks.
- Inhibiting and avoiding undesirable thermodynamic and kinetic pathways that may lead to unexpected material structures.

4.2. Computational Approach for Device and Process Development. In addition to maximum material/catalyst efficiency via high-efficiency material development approaches, engineering-level computation-based innovation is another key solution to decrease costs and energy requirements for realistic applications of large-scale CO₂ capture and conversion processes.

4.2.1. Device Design, Simulation and Optimization. Although effective capture materials with high selectivity and excellent stability can be identified by extensive experimental and microscopic-level computational investigations, a thorough evaluation at macroscopic levels is also required.

CFD-based Device Evaluation. Given an optimal material/catalyst for CO₂ capture/conversion, multiphase and single-phase device-scale CFD simulations for a predefined device configuration can predict and describe gas–liquid/gas–solid/gas–liquid–solid flow properties, outlet compositions, flow temperature, and pressure distributions. Development of reliable reaction-diffusion kinetics models and device-scale models are the requirements. The outcome would provide guidelines for deciding on the device geometry and operating parameters. For example, coarse-grid and multidimensional CFD simulations of cylindrical fluidized bed reactors for solids-based CO₂ capture have been studied to reveal flow fields under various operating conditions and cylindrical sizes.²⁴⁹ Several research contributions studying CFD simulations of CO₂ conversion in solid oxide electrolysis cells²⁵⁰ and different types of F-T synthesis and methanol synthesis reactors, such as bubble column slurry reactors,²⁵¹ multichannel reactors and packed bed reactors,²⁵² have been reported. Efficient CFD simulations of exothermic reactors can identify the optimal conditions that result in maximum yield of the major product while avoiding thermal deactivation of the catalyst. Compared to conventional reactors for CO₂ capture and conversion, simulation and analysis of photoreactors are more challenging due to the participation of radiation in the chemical reactions. Hydrodynamics of multiple phases, light intensity distribution, and reaction kinetics are key components of accurate CFD simulations for photochemical reactors.²⁵³

Device Dynamics. Dynamic first-principles models for devices that can be represented by ordinary/partial differential equations provide the basis for nonlinear analysis, dynamic optimization, and control system design.²⁵⁴ For example, one-dimensional partial differential equations for PSA for CO₂ capture using various solid sorbents such as MOFs, UiO-67, and MCM-41, have been defined to study dynamic concentration profiles.^{255,256} First-principles models of traditional TSA, models of rapid temperature swing adsorption (RTSA) have been developed and validated by experimental data to evaluate hollow fiber sorbents for CO₂ capture at an engineering level.²⁵⁷

Research in modeling and optimization of solvent-based/solid-sorbent-based postcombustion CO₂ capture processes, methanol synthesis, solid oxide electrolysis cells, and FT synthesis have been published.²⁵⁸ Complex first-principles mathematical models may lead to significant computational burden in control/optimization studies. Reduced order models

are potential options for ameliorating the computation speed while guaranteeing accuracy. For example, orthogonal collocation and proper orthogonal decomposition have recently been combined for extracting dynamic reduced order models from the original mathematical model, and this method has been employed to a bubbling fluidized bed adsorber for postcombustion CO₂ capture processes.²⁵⁹

Challenge. It is important to emphasize that for any first-principles models of processing units traditionally represented by ordinary/partial differential equations as well as CFD models, data sets of physical, thermodynamic, kinetic, and transport properties from experimental devices and even demonstration/industrial plants must be collected to validate and reconcile such models. Additionally, the following two conditions should be considered:

- How to enhance the computational efficiency via algorithmic and computing platforms innovation.
- How to guarantee the reliability of the mathematical model associated with new processes (i.e., air CO₂ capture and photochemical CO₂ conversion) because demonstration/pilot plants of these processes are limited or unavailable.

4.2.2. System Design, Synthesis and Evaluation. The technical and economic performance of new technologies for the CO₂ value chain are strongly dependent on the configuration, interconnections, operating conditions, and integration of various equipment into a process. Therefore, to screen rigorously and evaluate new technologies, it is important to guarantee that an optimal process is used for the evaluation. Mathematical-programming-based routes and simulation approaches have been extensively used to generate automatically design candidates for CO₂ capture/conversion processes and multiobjectively select the better ones.

Optimal Design of CO₂ Capture Processes. Nonlinear programming and mixed integer nonlinear programming are two main approaches to seek the optimal topology of CO₂ capture processes. With the aim of recovering 98% CO₂, a large-scale nonlinear programming framework has been developed to synthesize optimal PSA cycles for postcombustion and precombustion CO₂ capture, respectively.^{260,261} Indeed, an intractable optimization model may result if rigorous first-principle models of devices are directly included into the optimal synthesis framework as constraints. Thus, the opportunity and challenge is whether a simple surrogate model with high accuracy for certain complex processing unit can be obtained to remove the computational barriers.²⁶² For amine-functionalized silica-based CO₂ capture, a single fluidized bed adsorber is not enough for capturing at least 90% of the CO₂ from power plant flue gas. Therefore, a superstructure network (shown in Figure 13a) including a series of fluidized adsorbers and a series of fluidized regenerators has been developed. The algebraic surrogate models for adsorbers and regenerators are generated based on input–output data from Aspen Plus simulations of the individual devices. Solution of the superstructure optimization problem would identify the optimal number of adsorbers/regenerators and the number of trains in parallel.²⁶³ Similarly, accurate reduced order CFD models for gasification units and combined cycle combustion have been included in the optimization framework to identify the optimal flowsheet of the IGCC process.²⁶⁴

With regard to membrane-based CO₂ capture processes, either large membrane areas or a membrane with superior permeability

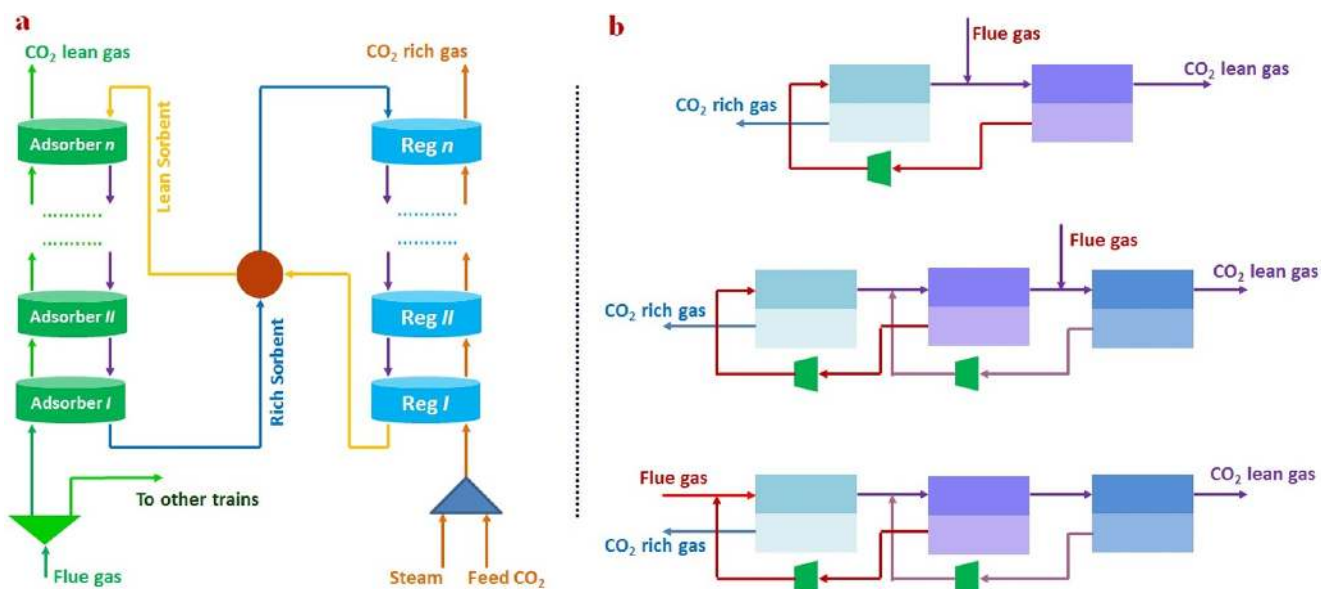


Figure 13. Superstructure of fluidized-bed-based and membrane-based CO₂ capture network.

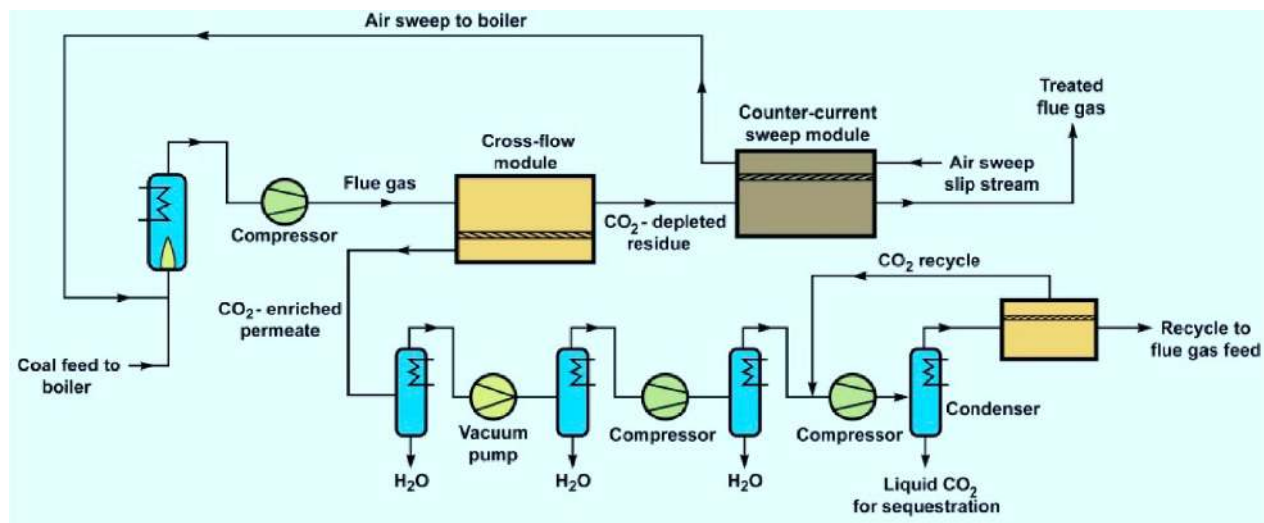


Figure 14. General flowsheet of the MTR polymeric membrane driven postcombustion CO₂ capture process (adopted from ref 265).

is needed to make the membrane-based capture process viable. For Polaris, which is commercially available, 0.5 to 1 million m² of membrane area is required for 90% CO₂ capture from the flue gas emitted by a 600 MWe plant. Clearly, a single-stage membrane process alone cannot produce high purity CO₂ in the permeate with 90% capture rate, regardless of the membrane selectivity. Using the Polaris of MTR, two modules in series (as shown in Figure 14) with countercurrent sweep has been proposed to offer “free” driving force to minimize the energy requirement.²⁶⁵ Actually, a complex membrane network (including modules in series, in parallel, or in hybrid means) shown in Figure 13b is required to achieve the set capture target with minimum energy and capital cost. The mathematical programming approach has been successfully employed to seek the optimal flowsheet of membrane processes for removing CO₂ from natural gas and biogas.^{266,267}

Optimal Design of CO₂ Conversion Processes. Recently, a very comprehensive superstructure network for upgrading CO₂ to valuable chemical products has been proposed.^{268,269}

This network problem could be defined as given CO₂ and a collection of resources, a list of desired products (methanol, polyurethane, formic acid, and dimethyl carbonate, etc.) and a network of processing steps with numerous alternatives for each step, perform a network superstructure optimization to obtain the best processing routes for an optimized set of products. The network is based on known and available information about catalysts, solvents, sorbents, reaction paths, etc. Compared to the mathematical programming approach, the simulation-based route has been more extensively used for the design and techno-economic analysis of the CO₂ conversion process. A great number of CO₂ conversion processes have been evaluated from economic and environmental perspectives via commercial simulators.

For methanol production from CO₂, the stand-alone dry-reforming-methanol synthesis process will emit more CO₂ than the input CO₂ due to the large amount of heat needed for reforming.²⁷⁰ For direct CO₂ hydrogenation, the large amount of H₂ required must be produced from renewable energy;

otherwise, the process is infeasible. However, the break-even price of methanol produced from CO₂ and H₂O using renewable energy (i.e., solar-thermal energy) is much higher than the current market price because these technologies have yet to reach mature levels.²⁷¹ Regardless of whether the desired product is methanol or Fischer–Tropsch liquids from CO₂, the primary contributor to the minimum selling price is the capital cost of the solar cell if the process is based on solar energy.²⁷² In addition to the above fossil fuel/renewable-energy-based thermochemical production routes, renewable-energy-based biochemical processes for reducing CO₂ to *n*-butanol and *n*-hexanol have also been studied.²⁷³

Challenge. Simulation-based and mathematical-programming-based approaches have been used to evaluate the economic and environmental impacts of CO₂ capture/conversion processes. Compared to CO₂ capture process design, there are fewer studies on the optimal design of CO₂ conversion processes. Currently, CO₂ capture and conversion processes are synthesized separately, but future designs should consider both simultaneously.

- Optimal design of integrated CO₂ capture–transportation–conversion process.
- Validate the optimal design for CO₂ capture/conversion via industrial studies.
- Development of simple algebraic models with high accuracy for the mathematical-programming-based design approach.
- Integrate the mathematical-programming-based approach with the simulation-based method to formulate a generic simulation-optimization platform for CO₂ value chain design.

4.2.3. Summary. Considerable progress has been made in the areas of particle/device/process modeling, device/process simulation and optimization for the CO₂ value chain. Various new mathematical models (2.5D CFD model, reduced order model, surrogate-model-based MINLP) have been proposed. The biggest barriers include model accuracy and computational efficiency. Collaboration with computer scientists should be initiated to develop advanced computing platforms for engineering-level large-scale computations. Future efforts should focus on the following unsolved questions:

- Comparison and validation of reduced order models with original first-principles model and experimental data.
- Integrate computational methods/approaches at device/process level with microscopic computation tools to achieve state-of-the-art generic computational platforms for CO₂ capture and conversion.

4.3. Conclusions on Computational Methods and Tools. For the development of a cost-effective large-scale CO₂ value chain, it is not sufficient to only improve the CO₂ conversion process or the capture process. The downstream CO₂ conversion and the upstream capture and transportation systems need to be integrated. The microscopic and macroscopic computational information should be shared and integrated. As the CO₂ value chain is a relatively new field and pilot/demonstration plants are limited, computational methods and tools complementary to experimental approaches will play an important role in reducing the time required for discovering, developing, and deploying the materials and processes on a large-scale. Comprehensive databases with information about conversion techniques, separation techniques, materials/catalysts employed, process descriptions, and much more need to be

linked with process simulation and optimization tools so that realistic large-scale problems can be considered.

5. FUTURE PERSPECTIVES ON A LARGE-SCALE CO₂ VALUE CHAIN

For developing and implementing a reliable and optimal large-scale CO₂ value chain, major indicators and requirements are listed as follows.

- Materials for CO₂ capture should demonstrate high selectivity/productivity, low energy requirements, excellent tolerance to impurities, and high long-term stability/durability under practical industrial conditions.
- Material synthesis approaches and manufacturing processes should be cost-effective and environmentally benign, and easily scalable to produce materials for the CO₂ capture process and catalysts for the CO₂ conversion process.
- The CO₂ capture process with optimal materials should be able to capture 90% CO₂ from stationary sources with minimal energy and electricity requirements.
- The energy content of the CO₂-derived products must be larger than the energy required for production.
- The amount of CO₂ emitted from the value chain must be less than the total amount of CO₂ converted.
- The CO₂ capture and conversion processes should exhibit excellent operability and be easily controlled.
- The CO₂ conversion process should be capable of responding to market fluctuations via multiproduct coproduction with low capital costs and environmental impacts.

As illustrated by Figure 15, the successful development and industrial deployment of large scale CO₂ capture and conversion processes requires highly multidisciplinary efforts encompassing fundamental scientific innovations, novel engineering exploitations, environmental considerations, and policy decisions at multiple time and length scales.

5.1. Computation-Experiment-System Framework for Material Discovery. With the aim of large-scale practical application, selectivity, stability, capacity, and tolerance to impurities are the key requirements when identifying materials for the CO₂ value chain. Materials demonstrating certain superior properties while other properties are extremely poor, may not be suitable for large-scale deployment. Currently, available approaches may not be able to discover novel materials meeting the desired target properties.

There is a need for an integrated framework that includes microscale computation/experimental screening and system evaluation. Currently, computational discovery and experimental screening are performed separately, which may provide unreasonable/erroneous results. For example, high selectivity and uptake capacity of advanced materials at the microscopic level may not guarantee the engineering-level purity and recovery targets for CO₂ capture.²⁷⁴ Benefiting from advances in computer science, mathematical techniques and high-throughput computational methodologies,^{241,275} in silico hierarchical computational frameworks integrating microscopic screening and macroscopic performance evaluation can theoretically avoid such potential conflicting conclusions,²⁷⁶ however, the identified materials may not have been validated through experimental screening yet. Additionally, approaches that combine experimental and microscopic computational screening have not yet been connected to system-level screening.

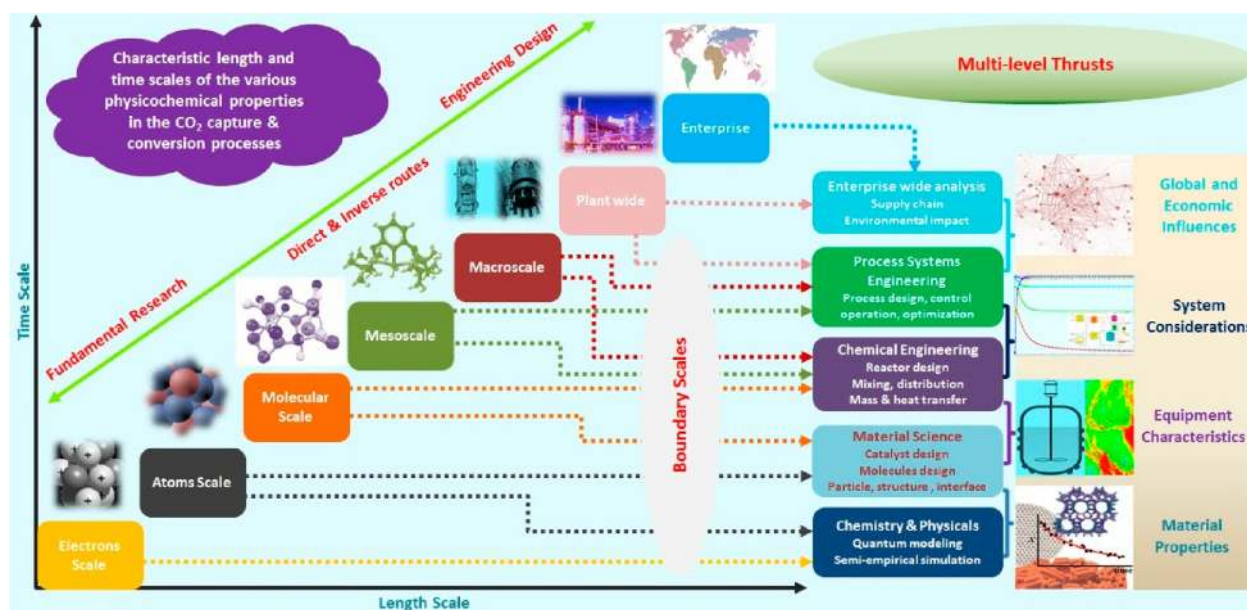


Figure 15. Multiscale multilevel approaches for CO₂ capture and conversion.

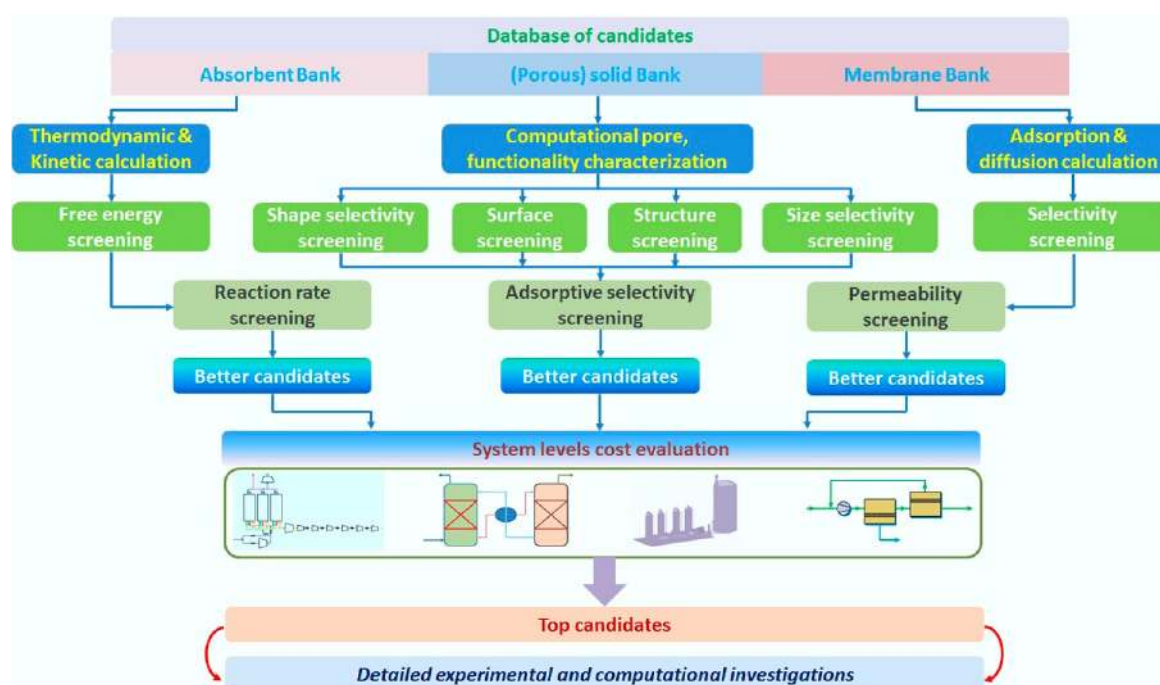


Figure 16. Multiscale screening framework for material discovery for CO₂ value chain.

If a list of candidates is known, the hierarchical screening framework shown in Figure 16 can be used to obtain suitable materials for the CO₂ value chain. With respect to inverse design for material discovery, Figure 17 represents an efficient framework. These holistic multiscale approaches provide an effective way to identify/develop knowledge of key factors determining the capture/catalytic performance of materials, thus enabling atomic scale design of tailored materials.

5.2. Materials Synthesis and Characterization. Irrespective of which framework is used for material discovery, the designed new materials must have high potential to be synthesized. It must also be emphasized that experimental studies under realistic conditions should be a central consideration in

creating materials for the CO₂ value chain. Advanced synthesis of new materials with controlled molecular functionalities to promote preferentially CO₂ capture and conversion is essential. Particularly, core–shell materials, novel carbon materials, MOFs with open sites, membrane constructs incorporating additional functional materials, and composite membranes call for advanced synthesis and processing methods.

Critical information from accurate characterization/analyses associated with materials for CO₂ capture and conversion can not only demonstrate efficacy of material synthesis and processing routes but also validate proposed reaction mechanisms and computational models. Therefore, as shown in Figure 18, state-of-the-art visualization tools should work together to gain deep

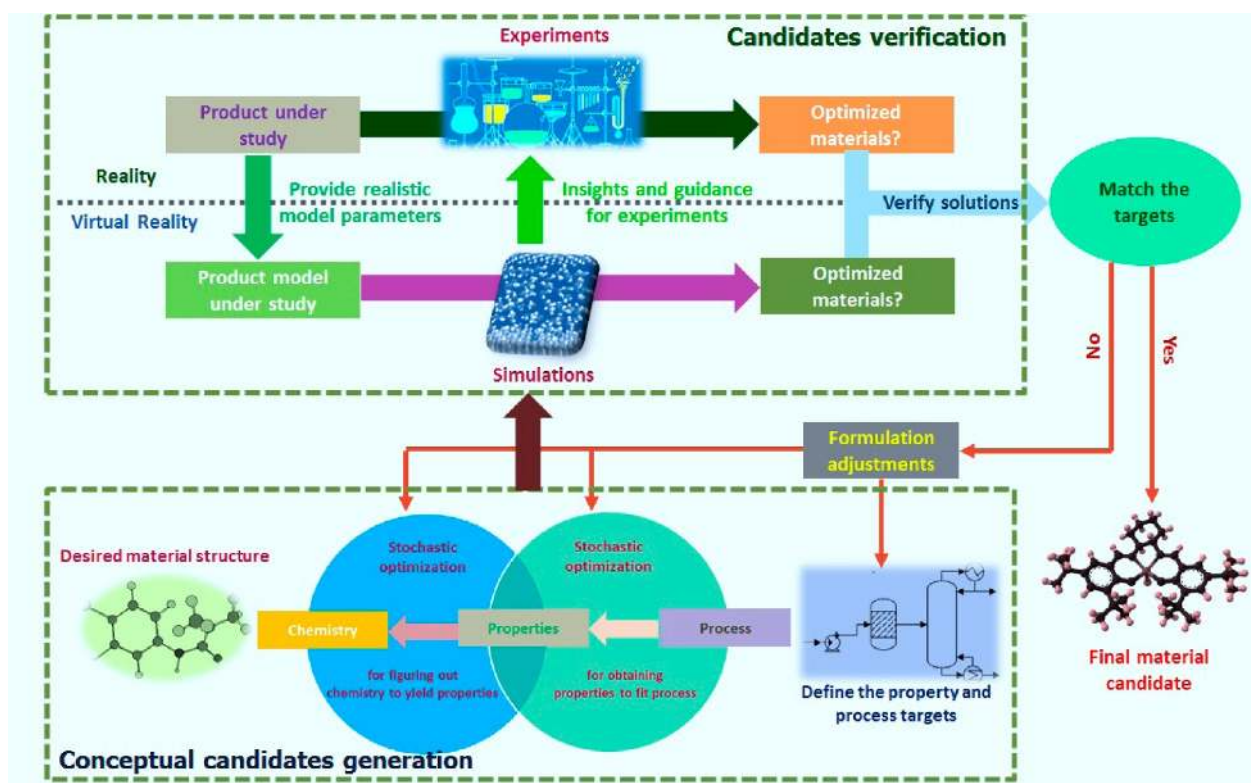


Figure 17. Holistic inverse design framework for novel material discovery.

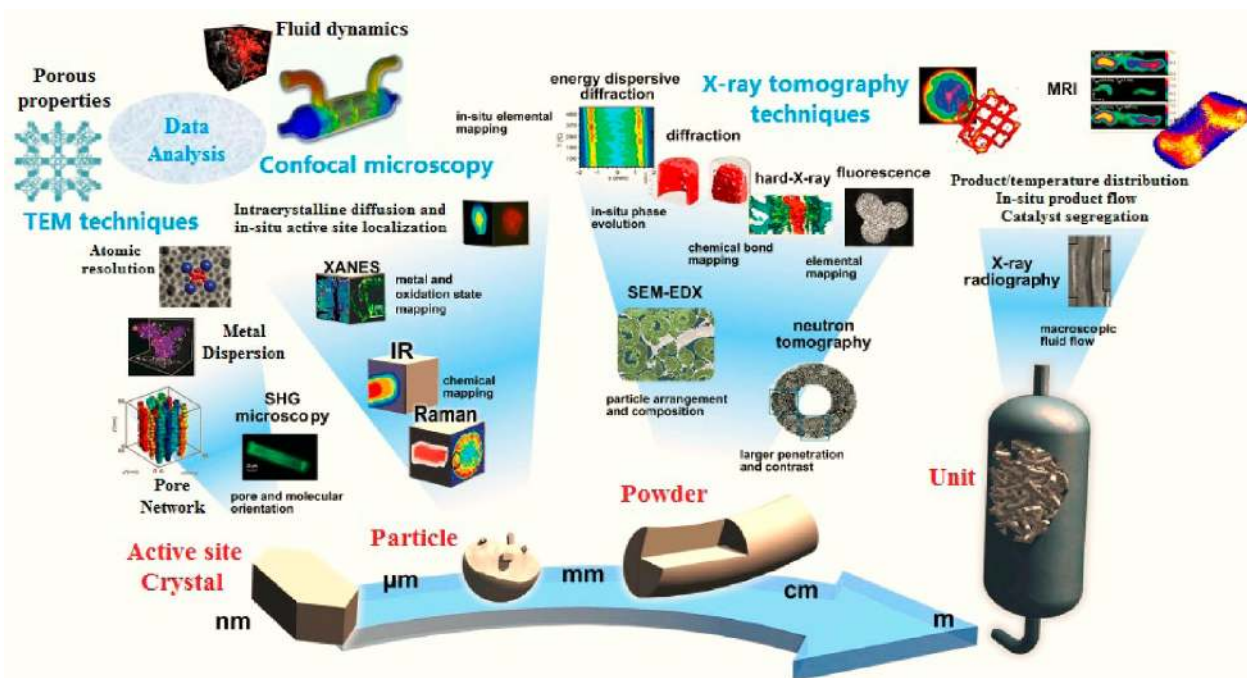


Figure 18. State-of-the-art visualization tools across multiple scales.

understanding of in situ temporal-/spatial-level structural²⁷⁷ and dynamic properties as well as guest–host interfaces and structural properties ranging from atomic/molecular level to device level.

5.3. Technology, Product, and Structure Consideration for CO₂ Value Chain. In contrast to biorenewable conversion processes, as illustrated by Figure 19a, the key aspect in developing a CO₂ conversion process is how to convert CO₂ to

intermediates. CO₂ conversion rate per pass and selectivity toward main products are two primary factors impacting the energy/cost efficiency of the overall CO₂ conversion process. It seems that current stand-alone photochemical and electrochemical processes cannot provide attractive economic performance for large-scale installations. For instance, the minimum selling price of methanol from the single-step photochemical

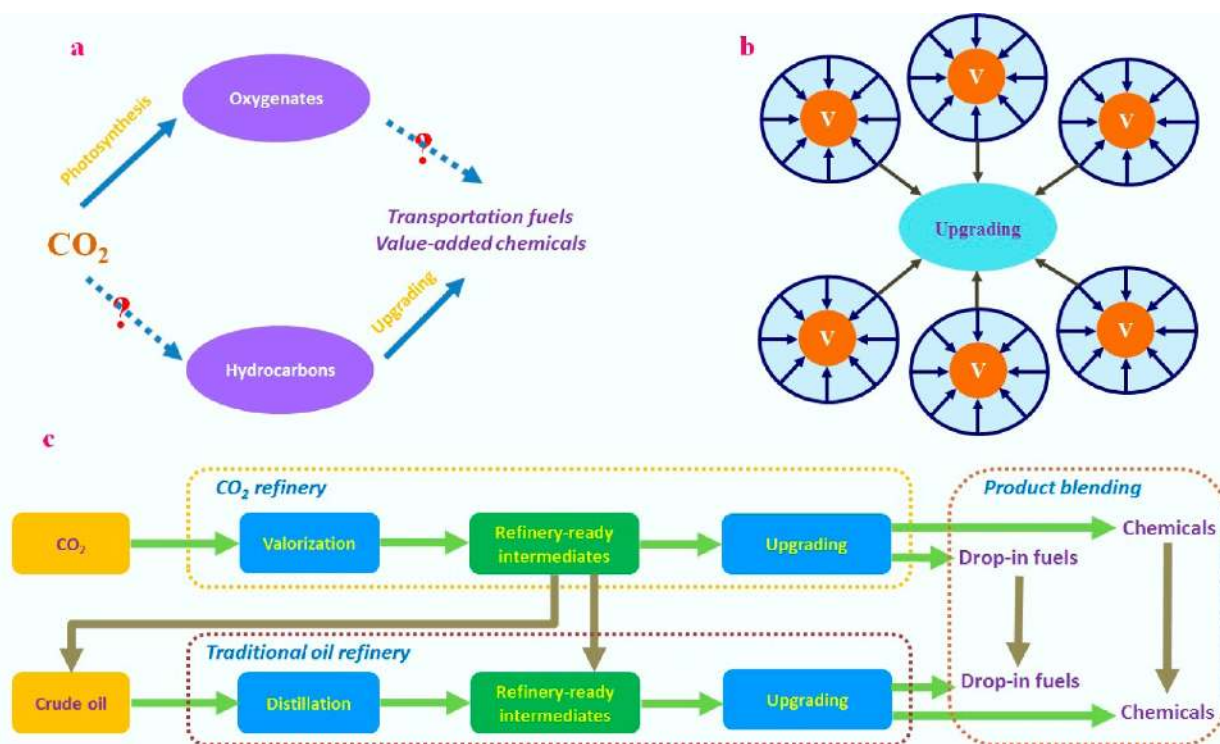


Figure 19. Structures and integration framework for CO₂ conversion.

conversion process, which is driven by a Ti-containing porous silica photocatalyst with a one-pass CO₂ conversion rate of 5% and methanol selectivity of 40%, is \$1.87 per kg.¹¹⁹ In the near/medium future, combining syngas production and catalytic upgrading is a promising alternative. Specifically, polygeneration of high value-added chemicals and high-quality liquid fuels along with lowering of the syngas production cost are two important requirements for a cost-effective CO₂ conversion process.

Different regions have unique specific resources and climate/geographical conditions that impact economic performance and energy resource choice/efficiency. If the CO₂ conversion site is located where ample wind energy or solar energy is available, then combining renewable electricity-driven H₂ production and RWGS may offer promising economics for syngas production. If the CO₂ conversion plant is close to a petrochemical/refinery plant, efficient utilization of any excess H₂ from such plants can economically provide a large amount of syngas. If the CO₂ conversion plant is near a natural gas or shale gas field, dry reforming may be a feasible and economical option.

The initial CO₂ valorization concept/pathway and downstream upgrading directly affects the overall economic performance. As shown by Figure 19b, distributed valorization and centralized upgrading are economical and viable CO₂ conversion structures. In addition to centralized upgrading sites, intermediates from the initial CO₂ valorization process can be sent to a traditional oil refinery (Figure 19c). For a successful integration, these intermediate streams must meet rigorous quality criteria and be free of contaminants that could poison the refinery catalysts or degrade the product. Therefore, high purity CO₂ from the capture site must be guaranteed. It must be emphasized that for integration with fossil-fuel-based sectors, the CO₂ emitted during the upgrading process must be separated and recycled.

5.4. Virtual CO₂ Capture and Conversion Plant with Limited Experimental Data Sets. Currently, CO₂ capture and

transformation technologies are still in their infancy. Data from pilot/demonstration plants for CO₂ capture and conversion are limited. No pilot plants exist for air CO₂ capture and photochemical CO₂ conversion. Furthermore, data from laboratory studies may not be sufficient as the thermodynamics and kinetics under laboratory conditions can be very different from the actual industrial conditions. Therefore, the question is whether a virtual pilot and demonstration plant can provide valuable data and insights for reconciling the reactor/separator design and even for improving the synthesis, processing and characterization of materials. Process systems engineering (PSE) researchers have the tools to build systematically virtual CO₂ capture/conversion plants including all components through simulation software such as Aspen Plus and gPROMS. The required thermodynamic and kinetic parameters can be extracted from limited experimental data. The effects of uncertainties and sensitivities associated with these parameters can be quantitatively and qualitatively analyzed through extensive large-scale simulation/optimization. All endogenous and exogenous influences can be investigated by running these virtual plants.

5.5. Systematic Considerations for CO₂ Value Chain. As illustrated by Figure 20, a cost-effective and energy-efficient CO₂ value chain including CO₂ capture, compression/transportation, and conversion not only requires fundamental scientific research at the microscopic level but also calls for comprehensive device-scale and system-scale innovations at the macroscopic level.

Investigating device-scale performance can guide scale-up and implementation of devices in process networks and lead to new unit development. Mathematical models validated by experimental data provide a reliable foundation for control system design and implementation. Indeed, such device-scale evaluations enable more effective screening of materials and concepts for CO₂ capture and conversion.

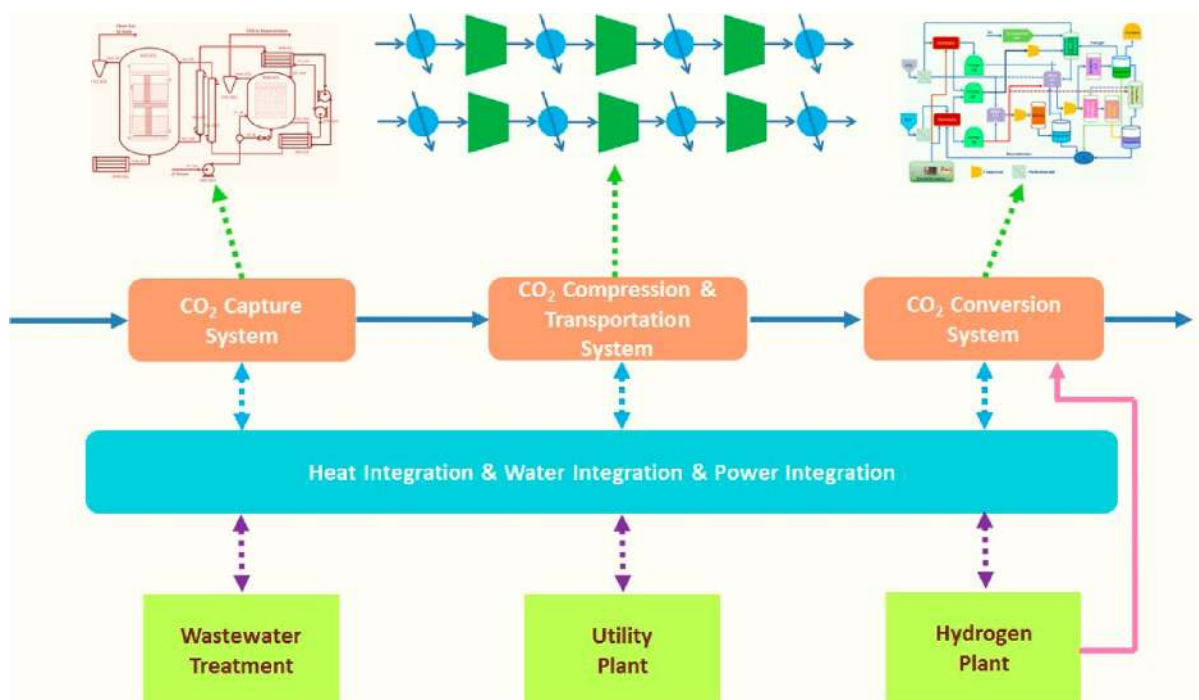


Figure 20. Schematic integrated CO₂ capture, transportation, and conversion site.

The integration of superstructure optimization and process simulation provides powerful methods to design and optimize smart CO₂ capture/conversion networks.²⁷⁸ For large-scale implementation, a single-stage hollow-fiber-based TSA process cannot produce high purity CO₂ with 90% CO₂ capture rate on its own. An optimal hollow-fiber-based CO₂ capture process requires a cost-effective and energy-efficient arrangement of modules in series, parallel or a hybrid of the two. Similarly, the integrated optimization framework can also be easily extended to optimize biochemical CO₂ conversion networks and PEM/SOEC/alkaline-based electrolysis networks due to the limited production capacity of a single unit. Optimal CO₂ capture/conversion process design enables identification of optimal equipment configurations, allow effective screening of materials and concepts, and identification of the types of devices/processes that should be considered for detailed modeling and analysis.

If the CO₂ capture and conversion plants are located close to each other, heat integration, power integration, and water integration across different units of these plants must be considered to maximize energy and water utilization as well as minimize waste generation/emissions. For example, if the amine-based technology is implemented for CO₂ capture and methanol synthesis/FT synthesis/mixed alcohols synthesis is selected for CO₂ valorization, the CO₂-rich amine streams can be heated by energy released from these exothermic reaction units through heat exchanger network synthesis. Alternatively, high-temperature steam produced from highly exothermic reaction units can generate electricity to support the integrated CO₂ capture and conversion site.

5.6. Enterprise Impacts. Various technologies have been proposed for capturing CO₂ from stationary sources and for converting the captured CO₂ to value-added products. However, without inclusion of CO₂ capture from ambient air, converting the captured CO₂ from stationary sources only improves fossil-fuel-derived carbon utilization. When CO₂ is converted to liquid fuels, the CO₂ conversion is just a temporary means of carbon

storage as the carbon contained in the produced liquid fuels will eventually be combusted and emitted as CO₂ to the atmosphere. If the CO₂ is transformed to value-added chemicals such as aromatics and olefins, CO₂ conversion can store carbon for a relatively long time. However, the CO₂ needed for producing such chemicals only accounts for a very small portion of the available resources as the market for olefins and aromatics is limited and significantly lower than for liquid fuels. Therefore, capturing CO₂ from ambient air from stationary sources, followed by polygeneration of valuable chemicals and liquid fuels are essential elements for achieving a cost-effective and sustainable carbon value chain. Specifically, efficient management of the upstream (CO₂ capture and transportation) and downstream operations (CO₂ conversion and product distribution) of the CO₂ supply chain is critical.

Life-cycle evaluation of CO₂ value chains is traditionally based on ad-hoc criteria such as amount of CO₂ utilized, amount of CO₂ captured, and simplified CO₂ balances, which may be useful when evaluating the environmental impact of potential CO₂ capture/conversion pathways at an early stage of design.^{279,280} However, such ad-hoc criteria-based quantitative environmental evaluations may not be a sufficient basis for decisions on large-scale implementations. Therefore, a holistic enterprise-level life-cycle assessment needs to be performed to assess correctly the environmental impacts of a CO₂ value chain and consequently to avoid misleading results. For example, life-cycle assessment of the CO₂ value chain should include the CO₂ source and the production of energy resources such as H₂ and electricity. Furthermore, life-cycle assessment should consider all products in the entire life cycle. The complete life-cycle assessment would set a reliable basis for the enterprise-level sustainability assessment composed of social, environmental, and economic factors. Multiobjective mixed integer nonlinear optimization-based approaches can be expected to provide an efficient tool for enterprise-level sustainability assessment of CO₂ value chains.

6. CONCLUSIONS

Current societal pressure for reduction of CO₂ emissions from continued utilization of diminishing fossil carbon provides an excellent opportunity for research in the discovery, development, and deployment of highly selective and flexible technologies for sustainable large-scale CO₂ capture and conversion. However, commercially available CO₂ capture and conversion technologies are limited. This paper has discussed the main obstacles for large-scale deployment of existing technologies for the capture/conversion of CO₂ and provided an overview of the computational methods/tools, which can complement experimental efforts. Promising future technologies and potential research directions have also been highlighted.

The successful implementation of CO₂ capture/conversion processes on a large scale can bridge the gap between fossil fuels and renewable energy. No singular solution is capable of addressing this complex problem. Interdisciplinary collaboration across materials, chemistry, catalysis, separation, process engineering, and environmental engineering is essential. Strategic integration of different technologies across broad temporal and spatial scales, from material design/synthesis at the molecular/atomic level to the plant-wide CO₂ capture and conversion process design at the macroscopic level and environmental/social impact assessment at the enterprise level, is necessary and provides a powerful means for accelerating the development, scale-up, and commercialization of cost-effective and energy-efficient large-scale CO₂ capture/conversion processes. Strategic partnerships between academia, industry, and governments are needed to take on this challenge, as it is too big to address by any one party.

■ ASSOCIATED CONTENT

● Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.iecr.5b03277.

CO₂ and N₂ permeation properties of select commercial polymeric membranes, List of existing CO₂ capture technologies together with their advantages and drawbacks, additional references (PDF).

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Notes

The authors declare no competing financial interest.

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