Recent Progress in the Integration of \( \text{CO}_2 \) Capture and Utilization

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Abstract: \( \text{CO}_2 \) emission is deemed to be mainly responsible for global warming. To reduce \( \text{CO}_2 \) emissions into the atmosphere and to use it as a carbon source, \( \text{CO}_2 \) capture and its conversion into valuable chemicals is greatly desirable. To reduce the transportation cost, the integration of the capture and utilization processes is a feasible option. Here, the recent progress in the integration of \( \text{CO}_2 \) capture and conversion is reviewed. The absorption, adsorption, and electrochemical separation capture processes integrated with several utilization processes, such as \( \text{CO}_2 \) hydrogenation, water–gas shift reaction, or dry methane reforming, is discussed in detail. The integration of capture and conversion over dual functional materials is also discussed. This review is aimed to encourage more efforts devoted to the integration of \( \text{CO}_2 \) capture and utilization, and thus contribute to carbon neutrality around the world.

Keywords: carbon neutrality; \( \text{CO}_2 \) capture; \( \text{CO}_2 \) conversion; integration

1. Introduction

Carbon dioxide capture, utilization, and storage (CCUS) are increasingly gaining global attention. The challenge is to meet the energy demand while balancing \( \text{CO}_2 \) emissions. Several solutions have been proposed to reduce the \( \text{CO}_2 \) emission, namely, increasing the utilization of eco-friendly energy sources, such as wind and solar energy, to improve the energy efficiency. However, the advancement of such technologies is currently still limited and can be an optimal option in the long-term. At present times, the CCUS technology is more effective and can be a short-term alternative.

\( \text{CO}_2 \) can be captured using various technologies, such as amine absorption, porous materials adsorption and membrane separation. Since \( \text{CO}_2 \) itself is a carbon source, it can be converted into valuable chemicals via dry methane reforming (DMR), \( \text{CO}_2 \) hydrogenation, reverse water–gas shift reaction, etc. There are excellent reviews on both the technologies [1–3]. However, the traditional \( \text{CO}_2 \) capture and utilization processes are separated, which inevitably increases the transportation cost. To reduce or even eliminate such cost, the integration of \( \text{CO}_2 \) capture and utilization is greatly desirable. This review focuses on the integration of \( \text{CO}_2 \) capture and utilization. The relevant processes and the materials involved will be discussed.

2. Integration of \( \text{CO}_2 \) Capture and Utilization

Integrated \( \text{CO}_2 \) capture and utilization aims to capture \( \text{CO}_2 \) from gas streams and other emission sources and convert it into valuable chemicals or energy sources. The key
is to find the match between the CO₂ separation process and the CO₂ utilization process, including the temperature and pressure, etc.

2.1. Integration of CO₂ Absorption and Conversion

CO₂ can be captured via physical or chemical absorption depending on the interaction between CO₂ and the absorbent. The former mainly utilizes the solubility of each gas component in the solvent whereas the latter involves chemical reactions between CO₂ and the absorbent. Chemical absorption is mostly employed with organic amine, hot potash, and liquid ammonia solvents considering its easy operation and mild working conditions [4]. Accordingly, it can be integrated with CO₂ hydrogenation for the production of formic acid or methanol.

Amine-based CO₂ capture and conversion integrated reactors consist of a series of amine sorbents and metal ions that form a pincer complex, such as pincer-pentaethylenehexamine (PEHA), pyrrolizidine, N,N,N′,N″,N″-pentamethyldiethylenetriamine (PMDTA) and polyethyleneimine (PEI). These are coupled with metal pincer-based homogeneous catalysts [5–8]. Due to the presence of multiple amine sites [9], PEI can be used as a superior CO₂ absorber [10], which can absorb both high and low concentrations of CO₂ [11]. Li et al. [12] used PEI/RhCl₃·3H₂O/CyPPh₂ to capture CO₂ and convert it in situ (Figure 1a). PEI absorbs CO₂ from air in an ethylene glycol solution containing PEI and converts it into amino formate esters and alkyl carbonate esters. CO₂ is hydrogenated in situ to form formate salts (TON = 260) in the presence of RhCl₃·3H₂O/CyPPh₂ demonstrating the first in situ CO₂ capture and conversion to formate. Multifunctional materials can be synthesized by modifying the PEI backbone with iminophosphine ligand functionality and subsequently metallizing it with Ir precursors. About 65% of the available primary amines on PEI can be modified to form iminophosphine/Ir (PN/Ir) for balanced CO₂ capture and conversion, resulting in higher formic acid yields. PEI with relatively lower molecular weight has better CO₂ capture ability and catalytic activity (Figure 1b) [13]. Kothandaraman et al. [14] reported, for the first time, a green and simplified method for in situ conversion of captured CO₂ to formate in aqueous media in the presence of Ru- and Fe-based pincer complexes without excess alkali, with yields of up to 95% of the formate.

Figure 1. (a) Proposed pathways of carbon capture and subsequent hydrogenation of the captured CO₂ [12]; (b) Formic acid yields in the hydrogenation of CO₂ catalyzed by the PEI-PN/Ir materials
as a function of temperature and MW of PEI for PEI600–PN/Ir (•), PEI1800–PN/Ir (•), and PEI3500–PN/Ir (•) [13]. (c) Multiple recycling of the catalyst in biphasic reaction mixture. Yield (%) of formate is relative to the amount of CO2 captured. Ru–PNP 1: Cat 1 = 10 μmol, T = 55 °C, H2 = 50 bar, 17.2 mmol diazabicyclo[2.2.2]octane (DABCO) + 3 mL H2O (CO2 captured each cycle = 15 mmol), 3 mL additional H2O–4 mL 2-Methyltetrahydrofuran (2-MeTHF) added for hydrogenation study. Fe–PNP 4: Cat 4 = 20 μmol, T = 55 °C, H2 = 50 bar, 17.2 mmol DABCO + 3 mL H2O (CO2 captured each cycle = 15 mmol), 3 mL additional H2O–4 mL 2-MeTHF added for hydrogenation study [14]. (d) Proposed reaction sequence for CO2 capture and in situ hydrogenation to CH3OH using a polycation [5].

In addition to formate, the captured CO2 can be converted into methanol. In 2015, Rezayee et al. [15] prepared methanol by tandem CO2 capture and in situ conversion of dimethylethylamine with homogeneous ruthenium complexes under basic conditions. Dimethylethylamine can react with CO2 and inhibit the formation of formic acid. The conversion of CO2 is >95% (Figure 1c). Moreover, Kothandaraman et al. [5] first proposed and demonstrated a system for capturing CO2 from air (~400 ppm) and converting it in situ (Figure 1d), which consisted of PEHA and Ru–PNP complex, with a methanol yield of 79%. Integrated systems for CO2 capture and conversion into methanol are still uncommon. The major obstacle is the harsh reaction conditions to produce methanol, which involves a high-pressure gas-phase catalyst reactor at relatively low temperatures of 200–300 °C and high pressures of 50–100 atm.

The amine-based materials offer the potential to capture and convert CO2 under mild conditions. Due to the relatively high CO2 capture capacity of PEI, it can directly capture CO2 from the air, which also removes the limitation of constructing CO2 capture equipment. However, the high selectivity of some materials to carbon dioxide poses a challenge for the regeneration of amines. Furthermore, the toxicity and corrosiveness of amine solvents limit their industrial application. To drive future research, it is essential to explore systems that are highly efficient and recyclable, enabling CCU to establish a reliable foundation for industrial applications.

2.2. CO2 Adsorption and Conversion Integration

Similar to absorption, adsorption separation can also be divided into chemisorption and physisorption according to the interaction between CO2 and the adsorbate, with the former forming covalent bonds whilst the latter forms bond with electrostatic attraction and van der Waals forces. Here, we mainly focus on the physisorption and the subsequent utilization of CO2.

Porous organic polymers (POPs) are a series of new two- or three-dimensional networked polymeric materials formed by covalent bonding of organic small molecule substrates through specific chemical reactions, usually with microporous, mesoporous or multistage pore structures. They have promising applications in separation, sensor and catalysis [16]. The ionic porous organic polymers (IPOPs) are generally classified as porous organic materials, whose backbone typically includes anions or cations. They can be divided into IPOPs with cationic moieties, IPOPs with anionic moieties, and IPOPs with zwitterionic moieties. Common cationic moieties include imidazolium, pyridinium, viologen, and quaternary phosphonium, whereas more common anionic moieties include tetrakis(phenyl)boration and tris(catecholate) phosphate. The inclusion of these ionic moieties in porous materials can enhance their CO2 capture capacity and catalyze the in situ CO2 conversion.

In 2011, tetrakis(4-ethynylphenyl)methane and diiodoimidazolium salts were used to prepare tubular microporous organic via Sonogashira coupling reaction networks bearing imidazolium salts (T-IM) (Figure 2a). The material, with a microporous structure of specific surface area (620 m2 g−1), shows good catalytic activity towards the conversion of CO2 to cyclic carbonates [17]. Wang et al. [18] utilized the Friedel–Crafts reaction to synthesize imidazole-based IPOPs. The specific surface area can reach up to 926 m2 g−1; however, its CO2 capture capacity is only 14.2 wt%. Nevertheless, the polymer exhibits
good stability and repeatability. Sun et al. [19] demonstrated, for the first time, the capture and in situ conversion of CO\textsubscript{2} into cyclic carbonates under relatively mild room temperature conditions using a metal-free solvent followed by a heterogeneous catalytic system. The effect of halogen anions (Cl, Br, and I) and quaternary phosphonium cations on the catalytic activity was investigated. The catalytic activity follows the order Cl\textsuperscript{−} > Br\textsuperscript{−} > I\textsuperscript{−} (Figure 2b), because the rate-controlling step of the reaction is ring opening by anion attack on the epoxide [20].

![Figure 2. (a) Preparation of porous organic networks bearing imidazolium salts [17]; (b) Yields of chloropropene carbonate from the cycloaddition of epichlorohydrin and CO\textsubscript{2} catalyzed by PIPs with corresponding QPs and PIP-Me-X, PIP-Et-X, and PIP-Bn-X (X = Cl, Br, and I). Reaction conditions: epichlorohydrin (1.0 g, 10.9 mmol), catalyst (0.05 mmol, based upon the quaternary phosphonium salt), 323 K, CO\textsubscript{2} (ambient pressure), and 24 h [19].](image)

In addition to IPOP, the porphyrin-based organic polymer (POP-TPP) can also be used. Xiao et al. [21] synthesized a hierarchically porous organic polymer (POP-TPP) by polymerizing vinyl-functionalized tetraphenylporphyrin monomer, and then metalated it with different metals (Co\textsuperscript{3+}, Zn\textsuperscript{2+}, and Mg\textsuperscript{2+}). The resulting heterogeneous catalysts have rich active sites and exhibit higher activity than the homogenous Co/TPP catalyst at relatively low CO\textsubscript{2} concentrations, primarily due to the favorable enrichment of CO\textsubscript{2} in the porous structure (micropores and nanochannels) of Co/POP-TPP. The TOF of the catalysts decreases in the following order: Co/POP-TPP (436 h\textsuperscript{−1}) > Zn/POP-TPP (326 h\textsuperscript{−1}) > Mg/POP-TPP (171 h\textsuperscript{−1}) (Table 1). Later, a series of high surface area hollow tubular metal (Al, Co, Fe, and Mn) porphyrin-based hypercrosslinked polymers (HCP) were synthesized via Friedel–Crafts alkylation reactions. Al-HCP can catalyze the formation of propylene carbonate with a selectivity of approximately 99% after only 1 h with 2.0 mol% TBAB catalyst [22].

Table 1. Cycloaddition of epichlorohydrin with CO\textsubscript{2} to form cyclic carbonate over various catalysts at 29 °C [21].

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalysts</th>
<th>Additives</th>
<th>Time (h)</th>
<th>Conv. (%) *</th>
<th>Select. (%) *</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 b</td>
<td>POP-TPP</td>
<td>n-BuNBr</td>
<td>24</td>
<td>52.1</td>
<td>&gt;99.0</td>
</tr>
<tr>
<td>2 c</td>
<td>Co/POP-TPP</td>
<td>n-BuNBr</td>
<td>24</td>
<td>95.6</td>
<td>99</td>
</tr>
<tr>
<td>3 c</td>
<td>Co/TPP</td>
<td>n-BuNBr</td>
<td>24</td>
<td>97.5</td>
<td>99</td>
</tr>
</tbody>
</table>
Metal–organic frameworks (MOFs) are porous crystalline materials formed by coordination between metal ions or metal clusters and organic ligands, which are characterized by high porosity, high surface area, tunable pore size and geometric configuration, and functionalizable pore surface [23]. Consequently, they can be employed for CO₂ capture and utilization. The imidazolium-based poly(ionic liquid)s (denoted as polyILs) and ortho-divinylbenzene were used as cross-linking agents to polymerize in the pores of MIL-101 (Figure 3a), resulting in polyILs@MIL-101 materials with dual functions of CO₂ capture and conversion [24]. For MOFs materials, ordered nanochannels can effectively promote the enrichment of CO₂ at the active sites and accelerate the CO₂ conversion; Lewis basic sites (LBSs) can supply electrons to activate CO₂ [25,26]. In order to restore the real CO₂ capture process, a CO₂ capture and in situ conversion system was designed by simulating the flue gas feed, where the lanthanide (III) complex of 1-vinylimidazole (Vim) was immobilized with DUT-5 by a combination of ligand and in situ polymerization (Figure 3b). This work opens up a general pathway for future research and validates the effectiveness of MOFs for practical applications in CO₂ capture and conversion [27].

Although the integrated materials have demonstrated good CO₂ capture and enrichment capabilities, their performance under the real industrial exhaust emissions that contain acidic gases, such as SOₓ, NOₓ, and steam, remain to be explored.

<table>
<thead>
<tr>
<th></th>
<th>Catalyst</th>
<th>Cross-linker</th>
<th>Time (h)</th>
<th>CO₂ (%)</th>
<th>O₂ (%)</th>
</tr>
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<tbody>
<tr>
<td>4</td>
<td>Co/POP-TPP</td>
<td>None</td>
<td>24</td>
<td>9.7</td>
<td>99</td>
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<tr>
<td>5</td>
<td>Co/TPP</td>
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<td>18.5</td>
<td>99</td>
</tr>
<tr>
<td>6</td>
<td>None</td>
<td>n-BuNBr</td>
<td>24</td>
<td>34</td>
<td>99</td>
</tr>
<tr>
<td>7</td>
<td>Co/POP-TPP</td>
<td>n-BuNBr</td>
<td>96</td>
<td>96.1</td>
<td>99</td>
</tr>
<tr>
<td>8</td>
<td>Co/POP-TPP</td>
<td>n-BuNBr</td>
<td>24</td>
<td>88.9</td>
<td>99</td>
</tr>
<tr>
<td>9</td>
<td>Zn/POP-TPP</td>
<td>n-BuNBr</td>
<td>24</td>
<td>93.2</td>
<td>&gt;99.0</td>
</tr>
<tr>
<td>10</td>
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<td>n-BuNBr</td>
<td>24</td>
<td>93.5</td>
<td>&gt;99.0</td>
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<tr>
<td>11</td>
<td>Mg/POP-TPP</td>
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</tr>
<tr>
<td>12</td>
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</tr>
<tr>
<td>13</td>
<td>Co/POP-TPP</td>
<td>n-BuNBr</td>
<td>24</td>
<td>93.6</td>
<td>99</td>
</tr>
</tbody>
</table>

Note: a Determined using GC analysis. b 48 mg of POP-TPP was used. c 50 mg of Co/POP-TPP (1.6 mg Co) or 19 mg of Co/TPP (1.6 mg Co) was used. d Co/POP-TPP catalyst (12.5 mg, 0.4 mg Co). e 50 mg of n-BuNBr. f 50 mg of Zn/POP-TPP (2.3 mg Zn) or 23.5 mg of Zn/TPP (2.3 mg Zn) was used. g 50 mg of Mg/POP-TPP (1.4 mg Mg) or 37.0 mg of Mg/TPP (1.4 mg Mg) was used. h Recycled for 18 times.

Figure 3. Schematic illustration of the preparation of (a) polyILs@MIL-101 [24] and (b) La–Vim/DUT-5 [27]. The “**” represents the monomer in the polymer.
2.3. CO$_2$: Electrochemical Membrane Separation and Conversion Integration

Electrochemical membrane separation is a technology that achieves gas separation through electrochemical reaction. The membrane can be mixed oxide ion-carbonate conductor (MOCC), such as Y$_{0.16}$Zr$_{0.84}$O$_{2-\delta}$-molten carbonate (YSZ-MC), Ce$_{0.8}$/Sm$_{0.2}$/O$_{2-\delta}$-MC (SDC-MC), Ce$_{1.0}$/Gd$_{1.0}$/O$_{2-\delta}$-MC (GDC-MC), and Bi$_{1.5}$/Y$_{0.3}$/Sm$_{0.2}$/O$_{3-\delta}$-MC (BYS-MC); mixed electron-carbonate conductor (MECC), such as stainless steel-MC (SS-MC), Ag-MC, and Ni-MC; or mixed oxide ion-electron-carbonate conductor (MOECC), such as La$_{0.6}$/Sr$_{0.4}$/Co$_{0.8}$/Fe$_{0.2}$/O$_{3-\delta}$-MC (LSCF-MC), and NiO-SDC-MC based on the charge carriers [2]. Generally, the carbonates (Li-Na-K-based) show high electrical conductivity and low viscosity only at relatively high temperature, e.g., >600 °C. Accordingly, it can be well integrated with the high temperature CO$_2$ utilization processes, such as DMR and reverse water-gas shift (RWGS) (Table 2).

Lin and co-workers first modeled the high temperature tube shell membrane reactor for separation and utilization of CO$_2$ from the flue gas and for simultaneous production of syngas using DMR. The membrane reactor is highly efficient for CCUS. The CH$_4$ conversion of 48.1% and an average CO$_2$ permeation flux of 1.52 mL cm$^{-2}$ min$^{-1}$ can be obtained at 800 °C with a 75 µm thick membrane and CH$_4$ space velocity of 3265 h$^{-1}$ [28]. Later, Anderson et al. [29] experimentally studied the integration of CO$_2$ separation and DMR with LSCF-MC membrane and Ni/γ-alumina catalyst. The CO$_2$ permeation rate above 750 °C matches the reaction rate of DMR catalyst, and the order of syngas production activity is blank system < LSCF combustion catalyst < Ni/γ-alumina reforming catalyst. The conversion of CO$_2$ and CH$_4$ is 88.5 and 8.1%, respectively, generating a syngas H$_2$:CO ratio of about 1 [30]. To improve the performance, Zhang et al. [31] employed MOCC membrane (GDC-MC) (Figure 4a), and NMP (Ni-MgO-1 wt% Pt) and LNF (La-Ni$_{0.6}$/Fe$_{0.4}$/O$_{3-\delta}$) catalysts. The yield of H$_2$ and CO and the conversion of CH$_4$ in the reactor with NMP catalyst is higher than that with LNF catalyst (Figure 4b,c), while the reactor with LNF catalyst shows better anti-coking performance and no significant degradation within 200 h. In addition, Zhang et al. [32] investigated the MECC membrane reactor (Ag-MC) coupled with dry-oxo methane reforming (DOMR) over an NMP catalyst. The CH$_4$ conversion is >82% and is stable over 115 h at 800 °C (Figure 4d). Similar reactor models can be applied to integrate CO$_2$ separation and oxidative dehydrogenation of ethane (ODHE) to produce ethylene [33]. CO$_2$ can react with H$_2$ to make the reaction of ethane dehydrogenation forward, which can increase the selectivity of O$_2$-ODHE to produce ethylene [33].
Figure 4. (a) Schematic illustration of a MOCC membrane reactor with a catalyst bed for electrochemical CO₂ capture and catalytic DMR. TPB: triple phase boundary [31]. (b) Effect of temperature on the DMR performance of a GDC–MC membrane reactor with an NMP catalyst [31]. (c) Effect of temperature on the DMR performance of a GDC–MC membrane reactor with an NMP catalyst and an LNF catalyst [31]. (d) Stability of DOMR performance of the Ag–MC MECC membrane reactor at 800 °C with NMP catalyst. Feed gas: 75 mL min⁻¹ N₂, 15 mL min⁻¹ CO₂, and 10 mL min⁻¹ O₂; sweep gas: 0.94 mL min⁻¹ CH₄ and 50 mL min⁻¹ Ar [32]. The dotted circles and arrows in the figure represent the axes corresponding to the curve.

The coupling of a dual-phase membrane reactor with a RWGS reaction was first reported by Chen et al. [34] to capture CO₂ and produce CO. Under a sweep gas condition of 1% H₂/He, the CO selectivity over LaNiO₃ (LNO) catalyst is >96% at 550–750 °C. Additionally, La₀.₉Ce₀.₁NiO₃−δ (LCNO) catalyst displays almost 100% CO selectivity and good thermal stability. The introduction of H₂ during the purge test enhances the permeation of CO₂. H₂O in dual-phase membrane systems can reduce the activation energy, possibly due to the conduction of hydroxide ions through the membrane [35].

The dual-phase membrane reactor can also increase the H₂ yield by removing CO₂. The concept of CO₂ removal was first applied to the steam reforming of methane reaction (SMR) to produce high concentration of H₂ by Wu et al. [36]. The asymmetric BYS-SDC-MC membrane reactor can convert methane into hydrogen via SMR reaction while simultaneously removing CO₂ to achieve a high concentration of hydrogen, with 84% CO₂ recovery (Figure 5a). The results of the mathematical model (Figure 5b) demonstrate that CO₂ recovery from SMR in the CO₂ permeated membrane reactor exceeds 99% and a pure H₂ gas stream without CO gas can be achieved [37].
The dual-phase membrane reactors can also be utilized for the oxidative coupling of methane (OCM) reaction. The high oxygen partial pressure in conventional OCM reactors often results in low C₂ selectivity. Li et al. [38] combined CO₂/O₂ transport membrane (CTM) and OCM reaction to build a new membrane reactor model (Figure 5c), which shows higher conversion of CH₄ than the traditional fixed-bed reactor model and better coking resistance. Based on this, Zhang et al. [39] developed a membrane reactor combining SDC-NiO-MC and 2%Mn-5%Na₂WO₄/SiO₂ catalyst. The co-captured CO₂/O₂ mixture converts CH₄ into C₂H₆ over the 2%Mn–5%Na₂WO₄/SiO₂ catalyst, followed by thermal cracking into C₂H₄ and H₂. In the presence of CO₂, the O₂ partial pressure is reduced, thereby reducing the possibility of re-oxidation of C₂ products, which leads to a higher C₂ selectivity.

Table 2. Summary of electrochemical membrane materials integrated reactors.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Catalyst</th>
<th>Reaction</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>La₀.₆Sr₀.₄Co₀.₈Fe₀.₂O₃-δ</td>
<td>Li-Na-K</td>
<td>10 wt%Ni-γ-Al₂O₃</td>
<td>DMR [29]</td>
</tr>
<tr>
<td>Ce₀.₆Gd₀.₄O₁.₉</td>
<td>Ni-MgO-1 wt%PtLaNi₀.₆Fe₀.₄O₃-δ</td>
<td>DMR [31]</td>
<td></td>
</tr>
</tbody>
</table>
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Note: Li-Na-K = Li2CO3: Na2CO3:K2CO3 with ratio of 42.5:32.5:25 mol%; Li-Na = Li2CO3: Na2CO3 with ratio of 52.48 mol%.

2.4. CO2 Capture and Conversion over Dual-Function Materials (DFMs)

Inorganic metal dual-functional materials (DFMs) combine the capture and conversion of CO2 into organic compounds. DFMs consist of the CO2 absorption component and the catalytic CO2 conversion component. The former is usually composed of alkali metal oxides or carbonates whilst the latter comprises metal-based catalysts, such as Ru, Rh, and Ni for DMR, dry ethane reforming (DER), RWGS reaction, and CO2 methanation [43–45]. Those processes can be well integrated with CO2 absorption considering their similar operating temperatures.

In 2018, Kim et al. [46] proposed and demonstrated the feasibility of using DFM to capture CO2 and convert it in situ with renewable CaO as an absorber of CO2 and Ni/MgO-Al2O3 as a catalyst for DMR. The concentration of CO2 in the exhaust gas is less than 0.08%, and the ratio of H2 to CO is 1.06. Tian et al. [47] synthesized CaO-Ni DFM using a sol–gel method. The ratio of H2 to CO is 1.1, which is similar to Kim’s results [46]. Methane decomposition can occur simultaneously during the reaction. The deposited carbon facilitates the reaction of CO2 with CaO-Ni; the CH4 conversion rate can reach 86%. Compared to other processes for DMR, the in situ consumption of CO2 on the catalyst surface promotes a positive shift of equilibrium in favor of CaCO3 decomposition, which allows the otherwise energy-intensive calcium cycling process to proceed at lower temperatures, thus further alleviating the deactivation problem during calcination. The energy consumed is 22% lower than the conventional consumption. In order to improve the activity and stability of Ni-CaO in the DMR reaction [48], CeO2 was added to the support, with a Ca:Ce molar ratio of 85:15. The resultant catalyst demonstrates good stability and maintains ~80–90% activity over nine cycles at 650 °C, which is over two times better than the material without CeO2 modification (Figure 6a). The dispersion of Ni and the reducibility of NiO are improved, enhancing the DMR activity. Due to the high mobility of lattice oxygen in CeO2, the CeO2 modification can inhibit the accumulation of non-active carbon on Ni.
In addition to DMR, the captured CO\(_2\) can be also converted into methane over DFM (Table 3). The Farrauto group is a pioneer in the study of CO\(_2\)-Met DFM. They prepared DFM using Ru as the metal catalyst, CaO as the CO\(_2\) absorbent, and γ-Al\(_2\)O\(_3\) as a carrier [51]. At 320 °C and 10% CO\(_2\)/N\(_2\), CO\(_2\) capture was carried out followed by methane production reaction for 2 h with 4% H\(_2\)/N\(_2\). The 5% Ru-10% CaO/γ-Al\(_2\)O\(_3\) exhibits the highest activity. In the CO\(_2\) capture cycle test with presence of steam, the purity of obtained methane can reach up to 99%. Duyar et al. [52,53] synthesized Ru- and Rh-based DFM from the nitrates of Ru and Rh, respectively, via impregnation. The Rh-based DFMs show better activity. However, their high cost limits large-scale application. In order to reduce the cost, Bermejo-Lopez et al. studied DFMs using Ni as the catalyst [54,55]. Ni-CaO/γ-Al\(_2\)O\(_3\) and Ni-Na\(_2\)CO\(_3\)/γ-Al\(_2\)O\(_3\) with different Ni loadings were synthesized via impregnation. The methane yield of 10% Ni-Na\(_2\)CO\(_3\)/γ-Al\(_2\)O\(_3\) is 186 μmol CH\(_4\) g\(^{-1}\) at 400 °C and it is 142 μmol CH\(_4\) g\(^{-1}\) at 520 °C for 15% Ni-CaO/γ-Al\(_2\)O\(_3\). In addition, Al-Mamoori et al. [56] prepared DFMs using Ni-impregnated CaO- and MgO-based double salts as CO\(_2\) absorber and catalyst, respectively, and γ-Al\(_2\)O\(_3\) as the carrier. The CO\(_2\) absorption was first saturated in a 10% CO\(_2\)/N\(_2\) atmosphere at 650 °C and 1 bar, and then a 5% C\(_3\)H\(_6\)/N\(_2\) mixture was passed into the reactor to react with CO\(_2\). The Ni@K(Ca)/γ-Al\(_2\)O\(_3\) system exhibits the highest CO\(_2\) absorption and 100% C\(_3\)H\(_6\) conversion. Nevertheless, Ni usually requires high reduction temperature and is very sensitive to O\(_2\) in the feed gas, and its long-term stability remains to be improved for the CO\(_2\)-Met reaction.
DFMs can also convert the captured CO$_2$ into valuable chemicals via RWGS reactions and ethane reforming. To investigate the effect of preparation methods on the performance of DFMs, Wang et al. [49] synthesized DFMs using three different methods, namely wet-mixing, acidification/impregnation, and acidification/impregnation combined with citric acid complexation. The Ni/CS-P30-C, prepared via acid pretreatment of carbide slag followed by citric acid complex, exhibits a high CO$_2$ sorption capacity (13.28 mmol g$^{-1}$ DFMs) and a great CO productivity (5.12 mmol g$^{-1}$ DFMs) at 650 ºC, and also demonstrates better CO$_2$ capture and in situ conversion (Figure 6b). Sun et al. [50] investigated the effect of Ce loading onto the Ca-Ni-based DFM on the performance of CO$_2$ capture and RWGS. The DFM with Ca:Ni:Ce = 1:0.1:0.033 (molar ratio) exhibits high cycling stability, and 100% CO selectivity (Figure 6c). The addition of CeO$_2$ effectively prevents the growth and aggregation of NiO and CaO species.

The primary concerns are catalyst deactivation during the reaction, carbon deposition, and matching capture and conversion rates, along with the requirement of evaluating the life cycle and economics of the integrated system. Therefore, further research is necessary in the future on aspects, such as reaction atmosphere, temperature, life cycle, economic analysis, and industrial applications.

3. Conclusions, Challenges and Opportunities

In summary, the integration of CO$_2$ capture and utilization is reviewed, namely the absorption, adsorption, and electrochemical separation capture processes integrated with several utilization processes. Initially, it is imperative to ensure that the operational conditions of the CO$_2$ capture process and the subsequent reaction process are fundamentally congruent, encompassing factors, such as temperature, pressure, pH, and other relevant parameters. Subsequently, the CO$_2$ absorption materials can be more effectively combined with the catalyst without impeding their respective performances. The point is to find the match between the operating temperature of both processes. To improve the performance of the integration system, one of the key factors is to achieve the match between the capture rate and the conversion rate. For example, in the MOCC and DMR system, matching the CO$_2$ separation rate of the MOCC membrane and the conversion rate over DMR catalyst is crucial. Unfortunately, such studies are very limited. Of course, improving the performance (activity, and stability) of the single process, either the capture or the conversion process, is desirable.

Although the integration of CO$_2$ capture and conversion is very promising to lower the CO$_2$ concentration in the atmosphere, there are still many challenges ahead. The amine-based absorption is currently employed by the industry, however, their toxicity, corrosiveness and high cost limit their further market applications. Suitable amine-based

<table>
<thead>
<tr>
<th>DFM</th>
<th>Condition (ºC)</th>
<th>Ref.</th>
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<tbody>
<tr>
<td>Ni-CaO/Al$_2$O$_3$</td>
<td>280–520 10% CO$_2$/Ar</td>
<td>[55]</td>
</tr>
<tr>
<td>Ni-Na$_2$CO$_3$/Al$_2$O$_3$</td>
<td>280–520 10% CO$_2$/Ar</td>
<td>[55]</td>
</tr>
<tr>
<td>Ni-Na$_2$O/Al$_2$O$_3$</td>
<td>320 7.5% CO$_2$/N$_2$ and 7.5% CO$_2$, 4.5% O$_2$, 15% H$_2$O/N$_2$</td>
<td>[52]</td>
</tr>
<tr>
<td>Ru-Na$_2$O/γ-Al$_2$O$_3$</td>
<td>320 15% CO$_2$/N$_2$</td>
<td>[57]</td>
</tr>
<tr>
<td>Rh-CaO/γ-Al$_2$O$_3$</td>
<td>320 10% CO$_2$/N$_2$</td>
<td>[57]</td>
</tr>
<tr>
<td>Ru-CaO/γ-Al$_2$O$_3$</td>
<td>280–400 1.4% CO$_2$/Ar and 11% CO$_2$/Ar</td>
<td>[54]</td>
</tr>
<tr>
<td>Ru-Na$_2$CO$_3$/γ-Al$_2$O$_3$</td>
<td>280–400 1.4% CO$_2$/Ar and 11% CO$_2$/A</td>
<td>[54]</td>
</tr>
<tr>
<td>Ru-CaO/γ-Al$_2$O$_3$</td>
<td>320 10% CO$_2$/air and 8% CO$_2$/21% H$_2$O/air</td>
<td>[51]</td>
</tr>
<tr>
<td>Ru-CaO/γ-Al$_2$O$_3$</td>
<td>320 10% CO$_2$/N$_2$</td>
<td>[57]</td>
</tr>
<tr>
<td>Ru-CaO/γ-Al$_2$O$_3$</td>
<td>320 7.5% CO$_2$, 4.5% O$_2$, 15% H$_2$O/N$_2$</td>
<td>[58]</td>
</tr>
<tr>
<td>Ru-Na$_2$CO$_3$/γ-Al$_2$O$_3$</td>
<td>320 7.5% CO$_2$/N$_2$ and 7.5% CO$_2$, 4.5% O$_2$, 15% H$_2$O/N$_2$</td>
<td>[59]</td>
</tr>
<tr>
<td>Ru-Na$_2$O/γ-Al$_2$O$_3$</td>
<td>250–350 7.5% CO$_2$, 4.5% O$_2$, 15% H$_2$O/N$_2$</td>
<td>[60]</td>
</tr>
</tbody>
</table>
or solid amine-based materials with low-energy, low-cost integrated CO$_2$ capture and conversion capabilities remain to be developed. For POP-based materials, their long-term and cycling stability, the impact of SO$_x$, NO$_x$, and other gases remain unclear. The production cost and complexity should be evaluated for future commercial promotion. The electrochemical membrane reactors integrated with catalysts is very promising for high-temperature CO$_2$ capture and conversion, but the CO$_2$ permeation flux and long-term stability are still needed to be improved. For the DFM-based materials, researching how to achieve the match between CO$_2$ capture and conversion is critical. The issues related with catalyst deactivation and operational life also remain to be solved.

To expedite innovation in the chemical industry, an integrated approach combining chemical experimentation with machine learning algorithms can be pursued. This paradigm shift will enable researchers to identify optimal materials faster and more efficiently, ultimately accelerating the pace of innovation in the global chemical industry.

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