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Recent advances in integrated CO₂ capture and utilization: a review

Shuzhuang Sun, Hongman Sun, Paul T. Williams* and Chunfei Wu*

CO₂ is one of the most important greenhouse gases leading to severe environmental issues. The increase of CO₂ emissions from the consumption of fossil fuels has received much research attention. One promising solution to reduce the impact of CO₂ is to integrate CO₂ capture and utilization (CCU), which shows many advantages compared to traditional separate CO₂ capture and utilization (CCU) processes. The CCU process shortens the path of CO₂ utilization such as CO₂ transportation and storage, and further negates the need for purification of products owing to the high conversion of CO₂. As an emerging integrated process, the improvement of CCU performance is crucial for future applications. This review analyses and discusses the influence of the key process parameters of CCU such as temperature, the presence of O₂ or H₂O in CO₂, GHSV etc., to provide guidance for future investigation. The development and application of dual functional materials (DFMs) in CCU are investigated and the roles and influence of interaction between adsorbents and catalysts are discussed. CaO showed superiority as an adsorbent to combine with CO₂ utilization catalysts owing to its low cost and high CO₂ capture capacity. The DFM system has opportunities to retard the deactivation of CaO owing to the presence of catalysts and the formed interaction. Nevertheless, there are several considerations from the industrial application perspective such as the reduction of overall cost and the possible post-processing requirements.

1. Introduction

The significant increase of CO₂ emissions, from 280 ppm in 1760 to 410 ppm in 2020, has become a serious global warming problem, resulting in a series of severe climate and environmental changes. The emissions of CO₂ are mainly attributed to fossil fuel consumption, in particular, the power generation sector emits the most CO₂, followed by industrial and transportation vehicles. Therefore, there is an urgent requirement for CO₂ reduction which is recognised by the Intergovernmental Panel on Climate Change (IPCC) and the introduction of relevant policies and regulations. The measures to reduce carbon emissions include the improvement of fuel energy efficiency, CO₂ capture, carbon storage and CO₂ conversion. CO₂ capture and storage (CCS) is a technology that decarbonises the use of fossil fuels in industries, such as power plants, steel works, cement kilns and oil refineries. CCS includes three main stages: (1) CO₂ capture; (2) transportation; (3) permanent CO₂ storage by mineralizing or injecting CO₂ into the ground or deep ocean. Porous materials such as activated carbon and zeolites are possible adsorbents for carbon capture. However, the poor adsorption selectivity of physical carbon capture limits its industrial application. Chemical adsorption is more promising and has already been applied in the CO₂ capture process, mainly including aqueous monoethanolamine (MEA) adsorption and calcium looping. The captured CO₂ can be released at a high concentration by temperature swing. As for the storage process, CCS could also be combined with the current fossil fuel extraction processes, for example, the underground injection of CO₂ for crude oil enhanced oil recovery. However, the high cost of separation, enrichment and transportation of CO₂ limits the deployment of CCS. Moreover, physical storage methods, such as underground or ocean injection, have negative impacts on natural ecology. Therefore, in addition to the development of CCS, increasing attention is being paid to the application of the captured CO₂ as a feedstock to produce valuable chemicals or fuels.

CO₂ capture and utilization (CCU) is a more sustainable process that can partially close the carbon cycle (as shown in Fig. 1). It is attractive to store the excess and uncertain supply of energy from renewable sources as stable chemical energy (i.e. methane, syngas or liquid chemicals) by integrating with CCU. Nowadays, there are many effective CO₂ utilization routes, including thermal-catalysis, photo-catalysis, electronic-catalysis, plasma-catalysis etc. Several reviews have summarized integrated CO₂ capture and low-temperature utilization, such as the production of formic acid, carbamate, urea, etc., using MOFs/COFs or other chemicals.
However, considering the large scale application in industry, materials with high cost are not reasonable for reducing CO₂ emissions. This review focuses more attention on high-temperature CO₂ capture and in situ utilization technologies using low-cost adsorbents (i.e. MgO and CaO) and commonly used catalysts, such as Ni, Fe-based or low loading of noble metal-based materials. Although high-temperature applications will bring additional energy consumption, ICCU can be operated isothermally and continuously by swinging the inlet gas. Furthermore, rapid and efficient carbon capture can be achieved using low-cost CaO or MgO at high temperatures. Industrially applicable CO₂ hydrogenation can be easily realized using the most common catalysts (i.e. Ni, Fe or Cu-based catalysts). As an important C1 chemical, CO₂ has attracted much attention for various end-use applications including CO₂ methanation, dry reforming of alkanes, the reverse water-gas shift reaction, etc. However, ICCU requires high CO₂ concentration for high conversion and inevitable product purification before it can be utilized for the production of useful products. As shown in Fig. 1, the traditional CCU process includes several steps to achieve ideal carbon capture and utilization, and in which the process would be also accompanied by undesirable high costs.

In recent years, increasing studies have been carried out on integrated CO₂ capture and utilization (ICCU) to reduce the cost of the overall process by eliminating transportation and storage of CO₂. As shown in Fig. 1, ICCU achieves in situ CO₂ adsorption, separation and conversion using dual-function materials (DFMs), which consist of CO₂ adsorbents and catalysts. First, DFMs can capture CO₂ from flue gas (~15 vol% CO₂) to effectively reduce carbon emissions. When the carbon capture process is completed, the feed gas is switched to a reducing agent (i.e. H₂, CH₄) for the conversion of the adsorbed CO₂ accomplished with the regeneration of the adsorbents. The reduction of CO₂ in ICCU is carried out under reducing agent-rich conditions, further avoiding the purification of products by significantly improving the conversion of CO₂. Compared with the traditional MEA adsorption and calcium looping process, the ICCU process avoids CO₂ desorption by temperature swing, which is considered as an energy-intensive process. What’s more, the effective in situ CO₂ utilization accompanied by adsorbent regeneration significantly simplifies the overall CO₂ utilization process.

The CO₂ adsorption, desorption and catalytic performances are significantly affected by the reaction temperature as well as the combination between catalysts and adsorbents. There are specific requirements for catalysts and adsorbents applied in DFMs, including the interaction between catalysts and adsorbents and the matching of adsorption/desorption efficiency and catalytic performance. ICCU has research gaps in both process optimization and catalytic mechanism investigation. In addition, the interactions and synergy effect between sorbents and catalysts of DFMs need significant research for better DFM design. This review critically introduces recent literature on CO₂ capture integrated with methanation, dry reforming of methane (DRM) and the reverse waste gas shift reaction (RWGS) from the perspectives of ICCU performance (i.e. CO₂ conversion, product yield, selectivity and process parameter optimization), CO₂ adsorbents (i.e. adsorbent system and understanding of the synergistic effect between catalysis and adsorption) and catalysts (i.e. catalytic system, active sites and catalytic mechanism). CO₂ utilization requires a specific reaction temperature which limits the selection and design of adsorbent in DFMs. In contrast, the presence of adsorbents promotes the performance of catalysts by assisting catalyst dispersion and provides close contact with CO₂ and catalysts. The interactions between adsorbents and catalysts are believed to play multifunctional roles in ICCU including promoting the stability of DFMs, providing effective catalytic sites and affecting the optimal parameters of ICCU. Furthermore, this review proposes research directions by pointing out the shortcomings of existing research from the perspective of industrial applications.

2. Progress in integrated CO₂ capture and methanation

Methane is the simplest hydrocarbon with the lowest C/H ratio, and is widely used in transportation, domestic heating and power plants because of its high calorific value (55.7 kJ g⁻¹), ready availability, low cost and clean combustion products. As shown in eqn (1), the conversion between CO₂ and CH₄, representing two important chemicals in C1 chemistry, has attracted great attention. Integrating CO₂ capture and methanation (ICCU-methanation) has advantages in improving the process and energy efficiency.

\[ \text{CO}_2 + 4\text{H}_2 = \text{CH}_4 + 2\text{H}_2\text{O} \quad \Delta H_{298\text{ K}} = -252.9 \text{ kJ mol}^{-1} \quad (1) \]

2.1 Influence of process parameters on ICCU-methanation

Temperature, reaction time, reducing agent parameters, the presence of O₂ and H₂O, etc., have large influences on the efficiency of ICCU-methanation which normally happens at an intermediate temperature (~300 °C). Table 1 summarizes the...
<table>
<thead>
<tr>
<th>DMs</th>
<th>Adsorption process</th>
<th>Hydrogenation process</th>
<th>CO₂ cap.</th>
<th>CO₂ conv.</th>
<th>CH₄ yield</th>
<th>CH₄ sel.</th>
<th>Cycle</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>5% Ru,10% CaO/γ-Al₂O₃</td>
<td>10% CO₂/N₂, 20 min, T = 320 °C, 1 atm</td>
<td>5% H₂/N₂, 20 min, T = 320 °C, 1 atm</td>
<td>0.4</td>
<td>82.7</td>
<td>0.30</td>
<td>NA</td>
<td>20 cycles</td>
<td>45</td>
</tr>
<tr>
<td>5% Ru,10% Na₂CO₃/γ-Al₂O₃</td>
<td>5% CO₂/N₂, 30 min, T = 320 °C, 1 atm</td>
<td>5% H₂/N₂, 30 min, T = 320 °C, 1 atm</td>
<td>0.5</td>
<td>NA</td>
<td>1.05</td>
<td>NA</td>
<td>3 cycles</td>
<td>46</td>
</tr>
<tr>
<td>5% Ru,10% CaO/Al₂O₃</td>
<td>7.5% CO₂ + 15% H₂O + 4.5% O₂ + 73% N₂, 20 min, T = 320 °C, 1 atm</td>
<td>5% H₂/N₂, 60 min, T = 320 °C, 1 atm</td>
<td>0.14</td>
<td>91.2</td>
<td>0.13</td>
<td>NA</td>
<td>10 cycles</td>
<td>44</td>
</tr>
<tr>
<td></td>
<td>Commercial Ni catalyst/Na₂O/Al₂O₃</td>
<td>15% CO₂/N₂, 100 ml min⁻¹, 1.34 atm, T = 350 °C</td>
<td>10% H₂/N₂, 100 ml min⁻¹, 1.34 atm, T = 350 °C</td>
<td>0.32</td>
<td>92</td>
<td>2.36 mol (kg⁻¹ h⁻¹)</td>
<td>NA</td>
<td>15 cycles</td>
</tr>
<tr>
<td>5% Ru,10% Na₂O/γ-Al₂O₃</td>
<td>7.5% CO₂ + 15% H₂O + 4.5% O₂/N₂, 300 ml min⁻¹, T = 320 °C, 1 atm</td>
<td>5% H₂/N₂, 300 ml min⁻¹, 30 min, T = 320 °C, 1 atm</td>
<td>0.29</td>
<td>73.3</td>
<td>0.21</td>
<td>NA</td>
<td>12 cycles</td>
<td>48</td>
</tr>
<tr>
<td>5% Ru,6.1% Na₂O/γ-Al₂O₃</td>
<td>7.5% CO₂ + 15% H₂O + 4.5% O₂/N₂, 15 min, GHSV = 521 h⁻¹, T = 300 °C, 1 atm</td>
<td>15% H₂/N₂, 15 min, GHSV = 1389 h⁻¹, T = 300 °C, 1 atm</td>
<td>0.44</td>
<td>80</td>
<td>0.35</td>
<td>NA</td>
<td>50 cycles</td>
<td>49</td>
</tr>
<tr>
<td>10% Ni,6.1% “Na₂O”/Al₂O₃</td>
<td>7.5% CO₂ + 15% H₂O + 4.5% O₂/N₂, 40 min, 30 ml min⁻¹, T = 320 °C</td>
<td>10% H₂/N₂, 60 min, 30 ml min⁻¹, T = 320 °C</td>
<td>0.43</td>
<td>71</td>
<td>0.30</td>
<td>NA</td>
<td>50</td>
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<tr>
<td>5% Ru,6.1% “Na₂O”/Al₂O₃</td>
<td>7.5% CO₂ + 15% H₂O + 4.5% O₂/N₂, 40 min 30 ml min⁻¹, T = 320 °C</td>
<td>10% H₂/N₂, 60 min, 30 ml min⁻¹, T = 320 °C</td>
<td>0.42</td>
<td>75</td>
<td>0.32</td>
<td>NA</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1% Ru,6.1% “Na₂O”/Al₂O₃</td>
<td>7.5% CO₂ + 15% H₂O + 4.5% O₂/N₂, 20 min, 100 ml min⁻¹, T = 320 °C, 1 atm</td>
<td>15% H₂/N₂, 200 ml min⁻¹, T = 320 °C</td>
<td>0.41</td>
<td>89</td>
<td>0.31</td>
<td>NA</td>
<td>20 cycles</td>
<td>51</td>
</tr>
<tr>
<td>1% Ru,10% Ni,6.1% “Na₂O”/Al₂O₃</td>
<td>Same as above</td>
<td>Same as above</td>
<td>0.52</td>
<td>81</td>
<td>0.38</td>
<td>NA</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.1% Ru,10% Ni,6.1% “Na₂O”/Al₂O₃</td>
<td>Same as above</td>
<td>Same as above</td>
<td>0.50</td>
<td>78</td>
<td>0.32</td>
<td>NA</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1% Pt, 10% Ni,6.1% “Na₂O”/Al₂O₃</td>
<td>Same as above</td>
<td>Same as above</td>
<td>0.35</td>
<td>87</td>
<td>0.25</td>
<td>NA</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.1% Pt, 10% Ni,6.1% “Na₂O”/Al₂O₃</td>
<td>Same as above</td>
<td>Same as above</td>
<td>0.39</td>
<td>52</td>
<td>0.16</td>
<td>NA</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.1% Pd, 10% Ni,6.1% “Na₂O”/Al₂O₃</td>
<td>Same as above</td>
<td>Same as above</td>
<td>0.47</td>
<td>57</td>
<td>0.18</td>
<td>NA</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ru₄Na₂CO₃</td>
<td>11% CO₂/Ar, 1 min, 1200 ml min⁻¹, T = 400 °C, 1 atm</td>
<td>10% H₂/Ar, 2 min, 1200 ml min⁻¹, T = 400 °C, 1 atm</td>
<td>0.42</td>
<td>94</td>
<td>0.39</td>
<td>&gt;99</td>
<td>52</td>
<td></td>
</tr>
<tr>
<td>Ru₄CaO</td>
<td>Same as above</td>
<td>Same as above</td>
<td>0.34</td>
<td>80</td>
<td>0.27</td>
<td>&gt;99</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10% Ni/CaO</td>
<td>10% CO₂ + 10% H₂O + 80% N₂, 120 min, 40 ml min⁻¹, T = 500 °C, 1 atm</td>
<td>90% H₂/N₂, 230 min, 40 ml min⁻¹, T = 500 °C, 1 atm</td>
<td>8.96</td>
<td>93</td>
<td>8.34</td>
<td>93</td>
<td>5 cycles</td>
<td>43</td>
</tr>
<tr>
<td>10% Ni/CaO</td>
<td>10% CO₂ + 10% H₂O + 80% N₂, 120 min, 40 ml min⁻¹, T = 600 °C, 1 atm</td>
<td>90% H₂/N₂, 230 min, 40 ml min⁻¹, T = 600 °C, 1 atm</td>
<td>15.49</td>
<td>96</td>
<td>14.94</td>
<td>96</td>
<td>NA</td>
<td></td>
</tr>
<tr>
<td>10% Ni/CaO</td>
<td>10% CO₂ + 10% H₂O + 80% N₂, 120 min, 40 ml min⁻¹, T = 700 °C, 1 atm</td>
<td>90% H₂/N₂, 230 min, 40 ml min⁻¹, T = 700 °C, 1 atm</td>
<td>16.22</td>
<td>83</td>
<td>4.7</td>
<td>29</td>
<td>NA</td>
<td></td>
</tr>
<tr>
<td>15% Ni 15% CaO/Al₂O₃</td>
<td>10% CO₂/Ar, 1 min, 1200 ml min⁻¹, T = 520 °C, 1 atm</td>
<td>10% H₂/Ar, 2 min, 1200 ml min⁻¹, T = 520 °C, 1 atm</td>
<td>0.16</td>
<td>88</td>
<td>0.14</td>
<td>87</td>
<td>41</td>
<td></td>
</tr>
<tr>
<td>15% Ni 15% Na₂CO₃/Al₂O₃</td>
<td>10% CO₂/Ar, 1 min, 1200 ml min⁻¹, T = 400 °C, 1 atm</td>
<td>10% H₂/Ar, 2 min, 1200 ml min⁻¹, T = 400 °C, 1 atm</td>
<td>0.21</td>
<td>88</td>
<td>0.19</td>
<td>86</td>
<td></td>
<td></td>
</tr>
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</table>

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performance of ICCU-methanation in relation to catalyst systems and reaction conditions. Most of those reported in the literature have been carried out under isothermal conditions and atmospheric pressure.

Temperature is one of the most important parameters in catalytic processes. For ICCU-methanation, Bermejo-López et al. investigated the influence of a wide temperature range, i.e. 200–600 °C, on ICCU-methanation using Ni–Ca/Al2O3 DFMs. The temperature showed a positive correlation with CO2 capture rate, CH4 yield and CO yield. A similar trend of temperature effects on the deactivation of catalysts by inducing excessive oxidation of metals. In addition, the presence of H2O and O2 in the feed gas production was observed owing to the oxidation of active metals. In addition, the presence of H2O and O2 in the feed gas decreases the capacity of CO2 capture by competitive adsorption.

Interestingly, the presence of H2O might not always play a negative role in ICCU. Miguel et al. found that H2O can participate in CO2 desorption, removing CO2 and promoting CH4 formation. The presence of H2O helped to dissolve K2CO3, which promoted the formation of bidentate carbonate in the CO2 adsorption process. The H2O generated in CO2 methanation was also suggested to be helpful for CO2 desorption, especially in the regeneration of sorbent sites.

2.2 Development of DFMs for ICCU-methanation

2.2.1 Adsorbents in DFMs for ICCU-methanation. In this section, the role of sorbents in DFMs is reviewed and discussed for ICCU-methanation. As shown in Table 1 and Fig. 2, Na2O, K2O, MgO and CaO are the most common sorbents for this process. CaO is widely used as a CO2 adsorbent owing to its

<table>
<thead>
<tr>
<th>DFMs</th>
<th>Adsorption process</th>
<th>Hydrogenation process</th>
<th>CO2 cap.</th>
<th>CO2 con.</th>
<th>CH4 yield</th>
<th>CH4 sel.</th>
<th>Cycle</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>2D-layered Ni-MgO-Al2O3, 2.0NiMgAl-LDOR</td>
<td>15% CO2/N2, 25 s, 70 ml min⁻¹, T = 250 °C, 1 atm</td>
<td>100% H2, 35 s, 70 ml min⁻¹, T = 250 °C, 1 atm</td>
<td>15.3</td>
<td>62</td>
<td>8.0</td>
<td>84</td>
<td>53</td>
<td></td>
</tr>
<tr>
<td>2% Ni/CoO2-CaO-physically mixed</td>
<td>15% CO2/N2, 60 min, 50 ml min⁻¹, T = 550 °C, 1 atm</td>
<td>100% H2, 60 min, 50 ml min⁻¹, T = 550 °C, 1 atm</td>
<td>4.25</td>
<td>79</td>
<td>3.36</td>
<td>NA</td>
<td>10 cycles</td>
<td>54</td>
</tr>
<tr>
<td>3% Ru/CoO2-MgO</td>
<td>65% CO2/N2, 60 min, 50 ml min⁻¹, T = 300 °C, 1 atm</td>
<td>5% H2/N2, 60 min, 50 ml min⁻¹, T = 300 °C, 1 atm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- CO2 capture capacity (mmol gDFM⁻¹).
- CO2 conversion (%).
- CH4 yield (mmol gDFM⁻¹).
- CH4 selectivity (%).
excellent theoretical adsorption capacity and low price. Due to sintering caused by volume change during the transformation between CaO and CaCO3, highly dispersed CaO could provide better stability than limestone derived CaO. Melis et al.45 dispersed CaO onto γ-Al2O3 and reported an increased CH4 yield, demonstrating that the spillover of CO2 from CaO to active sites occurred within DFMs. Due to the temperature limitation of CO2 methanation, Na2O and K2O are also popular for ICCU-CO2 methanation. Martha et al.50 studied dispersed alkaline adsorbents, including Na2O, CaO, K2O and MgO, and obtained enhanced methanation performance using Na2O and CaO (0.614, 0.610, 0.466 and 0.213 mmolCH4 gDFM–1 for Na2O, CaO, K2O and MgO, respectively). The doping of Na in γ-Al2O3 promotes the formation of Al–O– sites by promoting the formation of reversible bidentate and polydentate carbonates.37 Mertha et al.50 found that Na2O showed the fastest kinetics towards CH4 production compared to CaO, K2O and MgO. In addition, the Na2CO3-based DFMs showed acceptable stability (i.e. 27% decrease after 10 cycles) and the adsorption performance could be maintained by increasing the reduction time.38 The adsorption capacity of different alkali metal species varies as well. Bermejo-López et al.52 investigated oxides (CaO or Na2O) and hydrated oxides (Ca(OH)2 or NaOH) as CO2 storage sites, and reported that the former oxides were more reactive for CO2 adsorption.

Mg-based adsorbents are widely used in DFMs due to their low cost and medium adsorption temperature (~300 °C), as shown in Table 1 and Fig. 2. In addition, MgO does not have serious sintering issues like CaO, and the use of adsorbent carriers can be avoided to achieve more abundant adsorption capacity. Miguel et al.47 investigated the cycle stability of a Mg–Al hydrotalcite-based DFM. The authors obtained a decreased CO2 capacity in cycles, from 0.52 mmol g–1 to 0.32 mmol g–1, owing to the formation of irreversible bulk polydentate carbonate from unidentate and bridged carbonates. Thus promoters such as Li were used to stabilize MgO during the carbon capture stage of ICCU. Sun et al.54 applied alkaline metal (Li, Na, and K) promoted MgO in DFMs and obtained ~4 mmol gDFM–1 CO2 capacity after 10 cycles at a temperature below 300 °C. Attractively, Zhou et al.43 synthesized 2D layered Ni-MgO-Al2O3 nano-sheets and obtained prolonged cycling performance at low temperatures (~250 °C). However, the formation of difficult-to-reduce species, such as Ni–O–Mg and/or Ni–O–Al, suppressed the reducibility of low Ni-loading catalysts. Zhou et al.43 observed the formation of formate species in the CO2 capture process, which was formed from the hydrolysis of carbonate and/or bicarbonate.58 These formed formate species are desirable for methanation.59

The loading of adsorbents in DFMs can directly affect the capacity of CO2 capture. Melis et al.46 reported a positive correlation between adsorbent loading and CO2 capture capacity using dispersed K2CO3 as an adsorbent. However, a higher loading of the adsorbent could not always result in a better CO2 capture capacity when applying other alkali metal-based adsorbents. Melis et al.46 found an optimal loading of 10% for Na2CO3 and MgO. In addition to providing adsorption sites, the presence of sorbent could also promote catalytic performance in relation to the conversion of CO2. For example, Bermejo-López et al.52 reported that the dispersion of Ru or Ni was improved with the increase of adsorbent loading.

Different adsorbents show various performances for the process temperature of ICCU-methanation. Bermejo-López et al.52 observed that the performance of the CaO-based DFMs showed a significantly more positive correlation with the increase of temperature, while the medium temperature (i.e. 340 °C) is optimal for the Na2CO3-based DFMs. In the case of using CaO, a higher temperature was attributed to the decomposition of stable carbonates, while the Na2CO3 sorbent could release CO2 at a relatively lower temperature. The CaO and Na2CO3-based DFMs with low adsorbent loadings (i.e. 5 wt%) possess relatively weak basicity, results in decreased CO2 storage capacity and CH4 production at higher temperature.

In addition, the carriers used to disperse the adsorbent affect the adsorption performance in ICCU-methanation. For example, Martha et al.50 studied carrier materials, including CeO2, CeO2/ZrO2, Nazeolite-X, H-mordenite zeolite, SIC, SiO2 and ZrO2–Y and demonstrated that γ-Al2O3 was the most suitable carrier for DFMs. In addition to acting as a carrier, γ-Al2O3 could adsorb CO2 over Al2O3–OH groups.59 Laura et al.59 proposed that Al–O–Na+ species formed by the interaction between Na2O and Al2O3 allowed CO2 adsorption by the formation of bidentate carbonates over the sorbent surface using in situ DRIFTS (diffuse reflectance infrared fourier transform Spectroscopy) characterization.

As shown in Fig. 2, sorbents for CO2 capture could be dispersed into supports to enhance the stability of adsorbents, however, it could significantly reduce the capacity of CO2 capture owing to the reduction of adsorbent content. It is important to develop intermediate temperature adsorbents (~300 °C) with excellent stability and CO2 capture capacity for ICCU-methanation to increase the CO2 throughput of DFMs.

2.2.2 Catalysts in DFMs for ICCU-methanation. The role of catalytic sites in DFMs for ICCU-methanation is discussed in this section. It is known that the reduction of CO2 to CH4 is an eight-electron complicated process with significant kinetic
limitations. Therefore, CO₂ methanation requires suitable catalysts to achieve acceptable activity and selectivity. Metal-based catalysts, such as Ni, Ru and Rh, have been widely investigated for this process. As shown in Table 1, Ni was chosen as the methanation catalytic site by many researchers due to its high catalytic activity and relatively low cost. The effect of Ni loading in DFMs on ICCU-methanation was studied by Bermejo-López et al. In general, higher Ni loading promotes CO₂ capture and CH₄ generation owing to the closer contact between the adsorbents and metallic phase. Furthermore, increasing Ni loading could also slightly promote the decomposition of carbonates at lower temperatures.

Notably, the interaction between catalysts and adsorbents could positively affect ICCU-methanation. It was proposed that the reducibility of Ni species was enhanced in the presence of the adsorbent. The adsorbent impeded the close contact between Ni and Al₂O₃, weakening the interaction between both phases and favoring the formation of reducible NiO species.

However, there are shortcomings of Ni-based catalysts in DFMs for ICCU-methanation. When processing O₂-containing flue gas, Ni-based catalysts were oxidized and required much higher temperatures (i.e. 600 °C) to reduce. Other possible causes of the deactivation of Ni-based catalysts at low temperatures are the interaction of the metal particles with CO and the formation of mobile Ni subcarbonyls. Introducing other metals could help to decrease the reduction temperature of oxidized Ni-based DFMs in the step of CO₂ methanation. For example, Martha et al. introduced noble metals (Pt, Pb or Ru ≤ 1%) into Ni-based DFMs and obtained enhanced ICCU performance in the presence of H₂O and O₂. The authors also reported stable capacity of CO₂ capture (0.52 mmol g⁻¹cat) and CH₄ yield (0.38 mmol g⁻¹cat) after 20 cycles of capture and methanation using 1% Ru, 10% Ni, and 6.1%Na₂O/Al₂O₃ at 320 °C, indicating excellent long term stability of the Ru-promoted Ni-based DFM.

Noble metals could not only be used as a promoter of Ni-based DFMs, but also show impressive catalytic performance as the main active metal. Ru was the most promising one owing to its excellent catalytic activity of CO₂ methanation. Melis et al. applied 5 wt% Ru/Al₂O₃ DFMs in ICCU-methanation and obtained around 290 µmol g⁻¹cat CH₄ yield. Sun et al. utilized 10 wt% Ru/Al₂O₃-MgO and achieved higher CH₄ yield (7.07 mmol g⁻¹cat) and CO₂ conversion (89%) in ICCU-methanation. Ru-based DFMs have also shown excellent stable performance in ICCU. Wang et al. applied 5% Ru-6.1% Na₂O/Al₂O₃ DFMs and obtained 0.35 mmol g⁻¹cat CH₄ yield after 80 h operation. During the stability test, there was no loss of the BET surface area, CO₂ capture capacity and Ru dispersion. Ru showed acceptable performance in the presence of O₂. For example, Zheng et al. investigated the performance of Ru-Al₂O₃ DFMs under simulated flue gas conditions and proposed that Ru-based catalysts could be easily reduced after exposure to O₂-containing CO₂ flue gas. As shown in Fig. 3a, it is suggested that H₂ reduced oxidized Ru first, followed by the spillover of CO₂ from CaO to Ru. Lastly, the dissolved CO₂ at Ru sites formed CH₄ with the assistance of H₂. It is known that the loading of Ru is closely related to the catalytic performance. Bermejo-López et al. proposed that a higher Ru loading in Ru-10%Na₂O-Al₂O₃ resulted in an acceptable ICCU performance even at a notably lower temperature (i.e. 310 °C). However, there is an optimum Ru loading for ICCU-methanation. For example, Sun et al. reported that 10% Ru/Al₂O₃-MgO showed poorer stability than 5% Ru/Al₂O₃-MgO. It is mainly attributed to the presence of more oxygen vacancies that remained in 5% Ru/Al₂O₃-MgO. Better dispersion of Ru also promotes ICCU-methanation. For example, Melis et al. introduced Ru/CaO/Al₂O₃ DFMs for CO₂ methanation in ICCU. It was proposed that increasing the weight ratio of CaO to Ru promoted CO₂ spillover from CaO to Ru sites and then increased the performance of ICCU-methanation.

The distance between the active metals and the adsorbents also affects the performance of ICCU-methanation. Melis et al. compared physically mixed 10% Ru/Al₂O₃ and 10% CaO/Al₂O₃ with 10% Ru-10% CaO/Al₂O₃ for ICCU-methanation. The physically mixed DFMs showed a poor ICCU performance (0.12 g-mol CH₄/kg DFM) owing to the longer distance between active sites within the DFMs decreasing the effective CO₂ spillover. However, Sun et al. reported different conclusions by comparing physically mixed Ni/Al₂O₃-CaO with impregnated Ni/Al₂O₃ DFMs. The longer distance between Ni and CaO prevented the coverage of Ni from the formation of CaCO₃. Furthermore, the introduction of a CaO support would promote the dispersion of Ni and increase the performance of ICCU-methanation.

The addition of additives could promote the catalytic performance of DFMs for ICCU-methanation. For example, Stefano et al. introduced various alkali metals (Li, Na, and K carbonates vs. nitrates) into 1% Ru-Al₂O₃ DFMs and found that...
both the capture capacity of CO₂ and activity of methanation were enhanced \( \text{via} \) doping with Li (nitrates), which could react with Al₂O₃ to form a mixed spinel phase.

Investigating the catalytic mechanism helps to develop DFMs for ICCU-methanation. The mechanism and key intermediates of CH₄ formation from the ICCU process were studied by \textit{in situ} diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). Proaño et al.\textsuperscript{39} investigated the two steps of ICCU-methanation, including CO₂ adsorption and hydrogenation, over 5% Ru–6.1% Na₂O/Al₂O₃ DFMs. The authors found that CO₂ absorbed on the AlO\(^{−}\)–Na\(^{+}\) species formed bidentate carbonates (\textit{i.e.} 1st step in Fig. 3b), and then the adsorbed bicarbonates and bidentate carbonates spilled over onto the Ru-support interface during the CO₂ methanation process, with formates as reaction intermediates (\textit{i.e.} 2nd and 3rd steps in Fig. 3b), which is consistent with the results reported by Sun et al.\textsuperscript{34} In addition to the adsorbent, Ru as the catalytic site also showed the capacity of CO₂ adsorption,\textsuperscript{44,59} \textit{generating carbonyl groups.}\textsuperscript{54}

A lot of research has been conducted on the production of CH₄ by ICCU, but there is no valuable economic evaluation research in this field yet. However, ICCU-methanation can be combined with renewable H₂, and it still has a very broad prospect as integrated hydrogen storage and carbon-neutral solution.

### 3. Progress in integrated CO₂ capture and DRM

Compared to CO₂, the greenhouse effect of CH₄ is 22 times higher. Currently, CH₄ is widely used to produce H₂ by chemical looping reforming\textsuperscript{63} or steam methane reforming.\textsuperscript{54} Dry reforming of methane (DRM) utilizing these two major greenhouse gases, as shown in eqn (2), has received increasing attention in recent years.\textsuperscript{36,65} In addition to CH₄, C₂H₆ and other low-carbon alkanes could also be used for dry reforming.

Integrated CO₂ capture and dry reforming (ICCU-DRM) provides a promising solution for utilizing low carbon alkanes accompanied by the reduction of CO₂ emissions. Synthesizing liquid fuels or high-value hydrocarbons by Fischer–Tropsch synthesis using the products from the ICCU-DRM process could be a practical route for upgrading alkanes.

\[
\text{CH}_4 + \text{CO}_2 = 2\text{CO} + 2\text{H}_2 \quad \Delta H_{298}^{\circ} = +247 \text{ kJ mol}^{-1} \quad (2)
\]

#### 3.1 Influence of process parameters on ICCU-DRM

In this section, the influences of process parameters on the performance of ICCU-DRM are reviewed and discussed. As shown in Fig. 4a, there are various side reactions in ICCU-DRM, including CH₄ decomposition and the reverse-water-gas shift reaction (RWGS), which would generate coke on the surface of DFMs and affect the ratio of H₂/CO in the final product.

Temperature is one of the most effective parameters to influence the balance of DRM and side reactions. Molina-Ramírez et al.\textsuperscript{66} studied different temperatures (600–700 °C) of ICCU-DRM using a non-supported Ni–Ba bifunctional catalyst. The conversion of CH₄ increased with the increase of temperature (11.04% at 600 °C and 18.57% at 700 °C), while the selectivity to CO showed an opposite trend (14.89% at 600 °C and 4.69% at 700 °C). The side reactions, especially CH₄ decomposition, are favored at a higher temperature. The ratio of H₂/CO increased from 5.7 at 600 °C to 20.4 at 700 °C, which was accompanied by a significant carbon deposition on the surface of the DFMs. By applying dry reforming of ethane, Ahmed et al.\textsuperscript{67} investigated the influence of reaction temperature on Niₓ@[K–Ca]ₓ@[γ-Al₂O₃]ₙ over ICCU and found that the yield of syngas continuously increased with increasing temperature. Ethane conversion was positively correlated with temperature and could be fully converted at a higher
temperature (>650 °C), while the CO₂ conversion equilibrated at ~65% (>600 °C).

For ICCU-DRM, a higher temperature is not always preferred. Molina-Ramirez et al.⁴⁶ reported that the optimal temperature of Ni–Ba DFMs for CO₂ adsorption is 650 °C (0.37 mmol g⁻¹), capturing 0.23 and 0.13 mmol g⁻¹ CO₂ at 600 and 700 °C, respectively. It is suggested that a higher temperature enables the adsorption to approach equilibrium faster, but reduces the adsorption capacity at equilibrium. In terms of the desorption temperature for ICCU-DRM, Kim et al.¹ proposed that a reaction temperature of around 720 °C could steadily release CO₂. Too fast desorption would cause excessive CO₂ release at the initial time of the conversion stage, while slow desorption would decrease the overall efficiency of ICCU-DRM.

Reaction time is another important parameter in ICCU-DRM. For example, Kim et al.¹ studied different stages of ICCU through continuous online gas analysis. As shown in Fig. 4b, three reaction stages were proposed: (1) in the pre-breakthrough stage, CO₂ and CH₄ were almost fully converted, only 0.08% and 0.06% escaped, respectively. The produced syngas had a slightly higher H₂/CO ratio (0.37 mmol g⁻¹), capturing 0.23 and 0.13 mmol g⁻¹ CO₂ at 600 and 700 °C, respectively. It is suggested that a higher temperature enables the adsorption to approach equilibrium faster, but reduces the adsorption capacity at equilibrium. In terms of the desorption temperature for ICCU-DRM, Kim et al.¹ proposed that a reaction temperature of around 720 °C could steadily release CO₂. Too fast desorption would cause excessive CO₂ release at the initial time of the conversion stage, while slow desorption would decrease the overall efficiency of ICCU-DRM.

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3.2 Development progress of DFMs for ICCU-DRM

3.2.1 Adsorbents in DFMs for ICCU-DRM. The current CO₂ adsorbents applied in ICCU-DRM are mainly alkali metal oxides. High-temperature adsorbents, especially CaO-based materials, are the most commonly applied adsorbents owing to the thermodynamic requirements of DRM. However, the sintering of CaO is the most severe problem in this process. Kim et al.¹ applied CaO as the adsorbent and observed a significant decrease of CO₂ capture capacity after several cycles of ICCU-DRM. What’s more, the sintering of CaO would shorten the pre-breakthrough stage, as shown in Fig. 4b and 5a, which was suggested as the best stage for ICCU-DRM.

The presence of catalysts also affects the performance of adsorbents in ICCU-DRM. As shown in Fig. 5b, Tian et al.² reported that introducing catalysts in adsorbents significantly promoted the decomposition of CaCO₃ (~3 times faster). A similar promotion effect of catalysts on adsorbents was also reported by Ahmed et al.⁶⁷

Other adsorbents were also applied in ICCU-DRM, however with poor adsorption performance. For example, Molina-Ramirez et al.⁶⁶ synthesized a Ni–Ba unsupported DFM and obtained 0.232 mmol g⁻¹ capacity of CO₂ capture. In addition, MgO is not a suitable adsorbent for ICCU-DRM as Ahmed et al.⁶⁷ reported by Ahmed et al.⁶⁷. The presence of catalysts also affects the performance of adsorbents in ICCU-DRM. As shown in Fig. 5b, Tian et al.² reported that introducing catalysts in adsorbents significantly promoted the decomposition of CaCO₃ (~3 times faster). A similar promotion effect of catalysts on adsorbents was also reported by Ahmed et al.⁶⁷

3.2.2. Catalysts in DFMs for ICCU-DRM. As DRM requires a large amount of energy to process owing to its thermodynamic properties,⁴⁶ the introduction of catalysts such as Ni, Ru, Mo or Co-based catalysts can reduce the thermodynamic barrier and reduce the reaction temperature. The interaction between metals and adsorbents plays a key role in the ICCU-DRM process. Tian et al.² investigated two NiO forms in CaO–Ni bifunctional sorbent-catalysts by XPS and H₂-TPR. The proportion of interacted NiO increased from 64.0 to 80.7 atomic % with the increase of the Ca/Ni ratio. It was suggested that the presence of interacted NiO enhanced the ICCU-DRM. The authors also proposed that the sintering of catalysts could be prohibited by strengthening the metal–support interaction and/or the confinement effect of the support in the material matrix.

Fig. 5 (a) Molar flow rate and H₂/CO ratio of the effluent gas as a function of cycle number: (—) 1st, (−−−) 5th, and (−−−−) 10th cycles. The arrows highlight the trends with cycle number.¹ (b) Comparison of decarbonation kinetics as a function of time at 1073 K between CaL methane reforming and separate CaL processes.²
Fe-based catalysts also showed a good performance for ICCU-DRM. For example, Zhao et al. demonstrated a Ca–Fe chemical looping reforming process for ICCU. The authors observed the occurrence of the reaction between CH₄ and CaCO₃ and Fe₂O₃. As shown in Fig. 6b, in the 1st stage, the rapid full CH₄ oxidation reaction occurred and all Fe₂O₃ was changed into Fe₃O₄ (eqn (3) and eqn (4)) without CO generation. In the 2nd stage, the interaction between Fe-based oxygen storage materials and CO₂ adsorbents accompanied by the CH₄ reforming of CaCO₃ (eqn (5) and eqn (6)) achieved pure syngas production. Fe₂O₃ was gradually transformed into Fe and Fe₃O₄ with the grain size change in this stage. Along with further interactions, FeO rather than Fe was detected at the 3rd reaction stage. This might be attributed to the influence of the oxygen sources, including CO₂, lattice oxygen from the incompletely reduced Fe-based oxygen storage materials, or even lattice oxygen from the Al₂O₃ support. In the final stage, there was a reappearance of CaCO₃, which suggested that when the spine FeAl₂O₄ was reformed by methane, the unwanted byproduct CO₂ was recaptured by the carbonation reaction and thus utilized. In conclusion, the Ca–Fe DFM could restore its state and activity after oxidation and carbonation in flue gas and showed acceptable cycle stability.

\[
12\text{Fe}_2\text{O}_3 + \text{CH}_4 \rightarrow 8\text{Fe}_3\text{O}_4 + \text{CO}_2 + 2\text{H}_2\text{O} \quad \Delta G_{1173 \text{K}} = -532.33 \text{kJ mol}^{-1} \tag{3}
\]

\[
6\text{Fe}_2\text{O}_3 + \text{CH}_4 \rightarrow 4\text{Fe}_3\text{O}_4 + \text{CO}_2 + 2\text{H}_2 \quad \Delta G_{1173 \text{K}} = -300.08 \text{kJ mol}^{-1} \tag{4}
\]

\[
\text{CaCO}_3 + \text{CH}_4 \rightarrow \text{CaO} + 2\text{CO} + 2\text{H}_2 \quad \Delta G_{1173 \text{K}} = -74.96 \text{kJ mol}^{-1} \tag{5}
\]

\[
3\text{CaCO}_3 + \text{CH}_4 \rightarrow 3\text{CaO} + 4\text{CO} + 2\text{H}_2\text{O} \quad \Delta G_{1173 \text{K}} = -84.07 \text{kJ mol}^{-1} \tag{6}
\]

Introducing specific additives promotes ICCU-DRM. Ahmed et al. proposed that a K-introduced DFM showed better reducibility than a Na-introduced DFM by enhancing catalyst-support interactions. The promotion effect of Ni–Ca interactions was also verified by comparison with that of Ni–Mg DFMs. It was noted that with the introduction of alkaline metals, the ratio of H₂/CO was affected. For example, the K-introduced DFM showed a higher H₂/CO ratio owing to the higher conversion of dry reforming ethane and other side reactions.

4. Progress in integrated CO₂ capture and RWGS

The reverse water gas shift (RWGS) reaction is another important reaction in C₁-chemistry, which can connect with the production of valuable hydrocarbons through Fischer–Tropsch using the produced syngas. As shown in eqn (7), the RWGS reaction is an endothermic process with lower Gibbs energy than DRM. Although more expensive H₂ is used, the RWGS process has fewer side reactions than DRM. The integrated CO₂ capture and RWGS (ICCU-RWGS) process possesses the potential opportunity to directly produce pure syngas from flue gas.

\[
\text{CO}_2 + \text{H}_2 = \text{CO} + \text{H}_2\text{O} \quad \Delta H_{298 \text{K}} = +41.2 \text{kJ mol}^{-1} \tag{7}
\]

4.1 Influence of process parameters on ICCU-RWGS

In this section, several key parameters, including temperature, CO₂ concentration and the presence of contaminants, are reviewed for ICCU-RWGS. As shown in Fig. 7b, Luis et al. reported that a higher temperature improved both CO₂ conversion and CO selectivity owing to the endothermic properties of CO₂ capture and RWGS (ICCU-RWGS) process possesses the potential opportunity to directly produce pure syngas from flue gas.
RWGS. A similar trend in relation to the influence of temperature was also reported by Jo et al. using Ni/CaO DFMs. Shao et al. analyzed the temperature-programmed desorption of ICCU-RWGS using a Fe5Co5Mg10CaO DFM and found that CO could be generated at 550 °C, which was earlier than CO2 release. Within a certain temperature range (≤650 °C), operating ICCU-RWGS at a higher temperature could generate more CO due to the release of more CO2. However, too fast CO2 release rate at high temperatures could reduce its conversion to CO.

O2 and H2O are present in flue gas and affect the performance of ICCU-RWGS. Luís et al. investigated the influence of the presence of O2 or H2O on ICCU-RWGS using FeCrCu/K-hydrotalcite DFMs (Fig. 7a). The realistic conditions resulted in a poorer ICCU-RWGS performance owing to the deactivation of active sites (e.g. by surface oxidation or adsorption). The presence of H2O could suppress ICCU-RWGS by competitively adsorbing CO2 and affect RWGS equilibrium. Compared with the presence of H2O, the existing O2 has a more negative impact on ICCU-RWGS. The presence of O2 would significantly decrease CO2 conversion owing to the oxidation of catalytic sites.

The CO2 concentration could affect not only the performance of CO2 adsorption, but also the following RWGS process. With the increase of CO2 concentration from 5.8% to 9.5%, the efficiency of CO2 capture and CO2 conversion slightly decreased at temperatures under 450 °C, i.e. from 100% to 98% and from 80% to 67%, respectively. In contrast, CO selectivity was increased from 90% to 92%.

4.2 Development of DFM progress for ICCU-RWGS

4.2.1 Adsorbents in DFMs for ICCU-RWGS. CaO, a cheap and abundant adsorbent with excellent CO2 capacity, has been widely used in ICCU-RWGS due to its mature application in calcium chemical looping. In order to alleviate the sintering of CaO in cyclic adsorption and desorption, constructing a porous structure or better dispersion helps to improve the cycle performance of the adsorbent. The sol–gel method is a simple and effective way to synthesize porous materials, and was applied by Shao et al. and Sun et al.

In addition, introducing materials with high thermal stability also helps to limit excessive sintering of CaO. Sun et al. reported that introducing CeO2 as a physical barrier retarded the sintering of CaO. Similarly, Shao et al. achieved impressive cycle stability (no decrease after 10 cycles) by adding MgO into the DFMs.

Apart from the widely used CaO, hydrotalcite could also be a potential adsorbent, due to its structural stability at high temperatures. DFMs using hydrotalcite as an adsorbent showed excellent stability (stable after 750 cycles).

4.2.2 Catalysts in DFMs for ICCU-RWGS. RWGS is a popular research topic due to its potential industrial application in C1 chemistry. As shown in Fig. 8, noble metals [Pt81–83, Ru84, Au85,86 and Rh87], and Fe-based88–90, Ni-based91–96, Cu-based97–99 and Co-based100–102 metals are the most popular catalysts. It can be clearly observed that RWGS is favored at a higher reaction temperature. However, as shown in Fig. 8, there are obvious equilibrium limitations that limit the possibility of obtaining syngas with high purity from traditional RWGS. ICCU-RWGS can be the solution to facilitate the application of RWGS. Due to the unique reaction mechanism of ICCU, RWGS can be carried out at high hydrogen concentration, making it possible to obtain a high CO2 conversion and produce high-purity syngas.

In the existing ICCU-RWGS research work, transition metal-based catalysts have shown excellent catalytic performance. Shao et al. applied bimetallic Fe3+/Fe2+ and Co3+/Co2+ redox couples in a hierarchical porous CaO/MgO composite and achieved an excellent ICCU-RWGS performance. The bimetallic couples significantly lowered the electric potential difference of Fe3+/Fe2+ through the newly formed Fermi level in Fe5Co5Mg10CaO, which made the electron spillover easier to improve the catalytic activity. It was suggested that the same content of Fe and Co could achieve optimal ICCU-RWGS performance. The authors also proposed that Fe2+ was the active catalytic site, whereas Co acted as the catalytic promoter in Fe5Co5Mg10CaO DFMs. The catalytic process is as follows: firstly, CO2 was catalytically reduced to CO by magnetite (Fe3O4). Secondly, hematite (Fe2O3) was regenerated by H2 with Co as the promoter. The well-dispersed Fe can ensure the continuous and efficient process of this catalytic process. Luis et al. synthesized FeCrCu/K/MgO-Al2O3 DFMs for ICCU-RWGS under realistic conditions, and the key functions of Cu and K were suggested for efficient CO2 reduction and capture, respectively.

Supports can also play key roles in the catalytic process by promoting and stabilizing active catalytic sites. Sun et al. synthesized Ni–CeO2/CaO DFMs and achieved almost 100% CO selectivity, 51.8% CO2 conversion and remarkable cycle stability after 20 cycles of ICCU. The oxygen vacancies and interaction between Ni and CeO2 were believed to play key roles in promoting ICCU-RWGS. It was suggested that the formed interaction would effectively retard the agglomeration of NiO.
5. Progress in low temperature ICCU

The widely applied CO2 capture (i.e. MEA adsorption and calcium looping) and utilization (i.e. CO2 methanation and RWGS) consume a large amount of energy for sorbent regeneration and CO2 conversion. To overcome the drawbacks of the above processes, many researchers paid attention to photo-, electronic- and plasma-promoted catalytic processes. The integrated process can achieve promising performance under more mild conditions (ambient temperature and pressure) with the introduction of photo, electronic or plasma energy.

The traditional CO2 capture and utilization process can achieve excellent process efficiency. However, it needs either high temperature (>500 °C) or high pressure (>20 bar). Furthermore, these processes required relatively expensive reducing agents (i.e. H2 and CH4) to convert CO2. Alternatively, photo-catalytic reduction of CO2 with H2O has emerged as a promising option.118 Hybrid MgAl[LD0]/TiO2,118 NH2-UiO-66/TiO2,119 Mg(OH)2/CuO/Cu2O,120 etc. are applied in integrated CO2 capture and utilization and achieved promising results. Imidazolium ionic liquids, imidazolylidene heterocyclic carbones, and zeolitic imidazolate frameworks are also commonly used materials to realize this process.121 Integrated CO2 capture and photo-catalytic conversion provide a sustainable solution for CO2 emission reduction and utilization, which faces challenges in the improvement of catalytic efficiency.

The electrocatalytic CO2 reduction reaction (CO2RR) to produce valuable chemicals with renewable energy inputs is an attractive route to convert intermittent green energy sources.121-123 The CO2RR remains a huge challenge due to multiple proton and electron transfer processes and the chemical inactivity of CO2 molecules.124 Therefore, many researchers developed various finely designed materials to improve the efficiency of CO2 conversion. For example, Jiang et al.125 applied a wet chemistry and pyrolysis method to synthesize Sb SA/NC and achieved efficient formate production (faradaic efficiency of 94.0% at ~0.8 V vs. RHE). Recently, Lee et al.126 achieved an electrochemical upgrade of CO2 from amine capture solution, promising progress in large-scale application of integrated CO2 capture and electrocatalytic conversion. Electrocatalysis has a very high energy utilization efficiency. The possible drawbacks are the high requirements for the purity of the reactants to avoid the poisoning effect of impurities on the catalysts and equipment.126

Non-thermal plasma (NTP) catalyzed CO2 conversion has also become a promising method to significantly reduce the reaction temperature because plasma can activate CO2 at room temperatures and atmospheric pressure.29,32 In addition to DFMs containing adsorbents and catalysts, the membrane reactor is also gaining researchers’ attention. Chen et al.127 realized integrated CO2 membrane separation and NTP CO2 conversion with 91.8% carbon capture efficiency and 71.7% carbon utilization efficiency. This integrated process was also verified by Li et al.126 ICCU with NTP can achieve excellent reaction efficiency and scalable CO2 throughput. However, energy consumption related to NTP-ICCU needs to be particularly investigated.

Nowadays, low-temperature ICCU has gradually become a promising direction, and many finely designed materials are used in ICCU under mild conditions and have achieved excellent catalytic performance. CO2 reduction and neutralization should deal with a concentrated CO2 in industry (i.e. power plants and cement factories), which requires high CO2 throughput. High material costs may not be suitable for largescale processing, and the resistance to impurities in the CO2 sources will also determine the availability of related CCU technologies.

6. Conclusions and prospects

In this paper, we have critically reviewed the state-of-the-art progress in integrated high temperature CO2 capture and catalytic conversion, including CO2 methanation, DRM and RWGS, from the perspective of process parameters and catalytic materials. This process can not only decrease the overall CO2 utilization cost by eliminating CO2 enrichment and transportation, but also achieve outstanding CO2 conversion performance owing to the reducing agent rich conditions. However, there are several research gaps in this field that need to be addressed. For example, comprehensive considerations from the perspective of engineering are needed, including process design, and economic and technical analysis. The energy consumption for high temperature operations is noteworthy. Therefore, developing low-cost materials that can process ICCU at lower temperatures is promising. Furthermore, more research is needed for the development of dual functional catalysts for application in ICCU, including an in-depth understanding of the synergies between catalysts and adsorbents in addition to reaction intermediates.

For ICCU-methanation, an intermediate process temperature (~300 °C) shows better catalytic activity and CH4 selectivity. Ni-based DFMs can achieve excellent ICCU-methanation performance only in the absence of O2. The noble metal-based DFMs can obtain impressive ICCU performance, however, with inevitable high cost. The spillover of CO2 from adsorbents to catalytic sites is a key step for ICCU-methanation, which can be promoted by the interactions between adsorbents and catalysts. More research on the interactions within DFMs is necessary for a better understanding of the ICCU-methanation process and effective catalyst design. Furthermore, an economic evaluation will guide the development of ICCU-methanation.

For ICCU-DRM, a high temperature (>500 °C) is necessary to promote reactions. Therefore, both CaO and Ni are applicable and affordable. The reaction time is a critical parameter to control the coke formation in DFMs and optimize the H2/CO ratio of syngas in ICCU-DRM. The sintering of CaO and active metals at high temperatures is usually the main reason for the decrease of catalytic activity owing to the coverage of active sites and agglomeration of metals. The environmentally unfriendly CO generated from the coke in DFMs in the adsorption step is also worthy of attention.

ICCU-RWGS is a promising integrated process owing to its lower Gibbs energy and excellent selectivity of syngas. The
ICCU-RWGS process shows great potential for surpassing the equilibrium limitation of CO₂ conversion in traditional RWGS. The interaction among different components within DFMs plays multifunctional roles in ICCU-RWGS, including prohibiting the sintering of adsorbents, dispersing active metals and providing active sites. Apart from the investigation on the interaction within DFMs, the H₂/CO ratio of syngas from ICCU-RWGS also deserves more attention.

In conclusion, CO₂ capture and in situ catalytic conversion are still in their infancy. Reducing CO₂ emissions is not necessarily a high-cost industry. In contrast, it is possible to generate economic benefits through industrial integration. ICCU provides an economic CO₂ utilization strategy, which can integrate the abundant research on CO₂ capture and conversion and provide a solution for an urgent environmental need. The integration of CO₂ capture and utilization can also be expanded to other processes, including producing methanol or other valuable C₂+ chemicals. By producing more valuable chemicals, ICCU has the potential to be profitably accompanied by CO₂ emission reduction.

**Conflicts of interest**

There are no conflicts to declare.

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**Notes and references**

54 H. Sun, Y. Zhang, S. Guan, J. Huang and C. Wu, *J. CO₂ Util.*, 2020, 38, 262–272.