

REVIEW

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2021, 5, 4546Recent advances in integrated CO₂ capture and
utilization: a reviewShuzhuang Sun,^a Hongman Sun,^{lb} Paul T. Williams^{*c} and Chunfei Wu^{ld} ^{*a}

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 (ICCU), which shows many advantages compared to traditional separate CO₂ capture and utilization (CCU) processes. The ICCU 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 ICCU performance is crucial for future applications. This review analyses and discusses the influence of the key process parameters of ICCU 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 ICCU 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.

Received 25th May 2021

Accepted 20th July 2021

DOI: 10.1039/d1se00797a

rsc.li/sustainable-energy

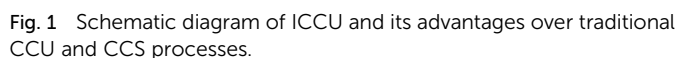
1. Introduction

The significant increase of CO₂ emissions, from 280 ppm in 1760 to 410 ppm in 2020,⁴ has become a serious global warming problem, resulting in a series of severe climate and environmental changes.⁵ The emissions of CO₂ are mainly attributed to fossil fuel consumption,⁶ in particular, the power generation sector emits the most CO₂, followed by industrial and transportation vehicles.^{6,7} 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.^{8,9} The measures to reduce carbon emissions include the improvement of fuel energy efficiency,¹⁰ CO₂ capture,^{11,12} carbon storage^{13,14} and CO₂ conversion.¹⁵ 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.⁶ CCS includes three main stages: (1) CO₂ capture; (2) transportation; (3) permanent CO₂ storage by mineralizing¹⁴ or injecting CO₂ into the ground or deep ocean.⁷ 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) adsorption¹⁶ and calcium looping.¹⁷ 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.^{16,18} However, the high cost of separation, enrichment¹⁹ and transportation of CO₂ (ref. 20) limits the deployment of CCS. Moreover, physical storage methods, such as underground or ocean injection, have negative impacts on natural ecology.²¹ 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.^{2,22}

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^{23,24}) by integrating with CCU.²⁵ Nowadays, there are many effective CO₂ utilization routes, including thermal-catalysis, photo-catalysis, electronic-catalysis,^{26–28} plasma-catalysis,²⁹ etc. Several reviews have summarized integrated CO₂ capture and low-temperature utilization, such as the production of formic acid, carbamate, urea,^{30,31} etc., using MOFs/COFs or other chemicals.^{15,31–33}

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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

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 water 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.

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 CO_2 and CH_4 , representing two important chemicals in C1 chemistry, has attracted great attention. Integrating CO_2 capture and methanation (CCU-methanation) has advantages in improving the process and energy efficiency.



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 1 The catalyst system, performance and reaction condition details of reported integrated CO₂ capture and methanation research work

DFMs	Adsorption process	Hydrogenation process	CO ₂ cap. ^a	CO ₂ con. ^b	CH ₄ yield ^c	CH ₄ sel. ^d	Cycle	Ref.
5% Ru,10% CaO/ γ-Al ₂ O ₃	10% CO ₂ /N ₂ , 20 min, <i>T</i> = 320 °C, 1 atm	5% H ₂ /N ₂ , 20 min, <i>T</i> = 320 °C, 1 atm	0.4	82.7	0.30	NA	20 cycles	45
5% Ru,10% Na ₂ CO ₃ /γ-Al ₂ O ₃	5% CO ₂ /N ₂ , 30 min, <i>T</i> = 320 °C, 1 atm	5% H ₂ /N ₂ , 30 min, <i>T</i> = 320 °C, 1 atm	0.5	NA	1.05	NA	3 cycles	46
5% Ru,10% CaO/ Al ₂ O ₃ pellets	7.5% CO ₂ + 15% H ₂ O + 4.5% O ₂ + 73% N ₂ , 20 min, <i>T</i> = 320 °C, 1 atm	5% H ₂ /N ₂ , 60 min, <i>T</i> = 320 °C, 1 atm	0.14	91.2	0.13	NA	10 cycles	44
Commercial Ni catalyst/ hydrotalcite	15% CO ₂ /N ₂ , 100 ml min ⁻¹ , 1.34 atm, <i>T</i> = 350 °C	10% H ₂ /N ₂ , 100 ml min ⁻¹ , 1.34 atm, <i>T</i> = 350 °C	0.32	92	2.36 mol (kg ⁻¹ h ⁻¹)	NA	15 cycles	47
5% Ru,10% Na ₂ CO ₃ /Al ₂ O ₃	7.5% CO ₂ + 15% H ₂ O + 4.5% O ₂ /N ₂ , 300 ml min ⁻¹ , <i>T</i> = 320 °C, 1 atm	5% H ₂ /N ₂ , 300 ml min ⁻¹ , 30 min, <i>T</i> = 320 °C, 1 atm	0.29	73.3	0.21	NA	12 cycles	48
5% Ru,6.1% Na ₂ O/γ-Al ₂ O ₃	7.5% CO ₂ + 15% H ₂ O + 4.5% O ₂ /N ₂ , 15 min, GHSV = 521 h ⁻¹ , <i>T</i> = 300 °C, 1 atm	15% H ₂ /N ₂ , 15 min, GHSV = 1389 h ⁻¹ , <i>T</i> = 300 °C, 1 atm	0.44	80	0.35	NA	50 cycles	49
10% Ni,6.1% “Na ₂ O”/Al ₂ O ₃	7.5% CO ₂ + 15% H ₂ O + 4.5% O ₂ /N ₂ , 40 min, 30 ml min ⁻¹ , <i>T</i> = 320 °C	10% H ₂ /N ₂ , 60 min, 30 ml min ⁻¹ , <i>T</i> = 320 °C	0.43	71	0.30	NA		50
5% Ru,6.1% “Na ₂ O”/Al ₂ O ₃	7.5% CO ₂ + 15% H ₂ O + 4.5% O ₂ /N ₂ , 40 min 30 ml min ⁻¹ , <i>T</i> = 320 °C	10% H ₂ /N ₂ , 60 min, 30 ml min ⁻¹ , <i>T</i> = 320 °C	0.42	75	0.32	NA		
1% Ru,6.1% “Na ₂ O”/Al ₂ O ₃	7.5% CO ₂ + 15% H ₂ O + 4.5% O ₂ /N ₂ , 20 min, 100 ml min ⁻¹ , <i>T</i> = 320 °C, 1 atm	15% H ₂ /N ₂ , 200 ml min ⁻¹ , <i>T</i> = 320 °C	0.41	89	0.31	NA	20 cycles	51
1% Ru,10% Ni,6.1% “Na ₂ O”/Al ₂ O ₃	Same as above	Same as above	0.52	81	0.38	NA		
0.1% Ru,10% Ni, 6.1% “Na ₂ O”/Al ₂ O ₃	Same as above	Same as above	0.50	78	0.32	NA		
1% Pt, 10% Ni, 6.1% “Na ₂ O”/Al ₂ O ₃	Same as above	Same as above	0.35	87	0.25	NA		
0.1% Pt, 10% Ni, 6.1% “Na ₂ O”/Al ₂ O ₃	Same as above	Same as above	0.39	52	0.16	NA		
0.1% Pd, 10% Ni, 6.1% “Na ₂ O”/Al ₂ O ₃	Same as above	Same as above	0.47	57	0.18	NA		
Ru ₁₀ Na ₂ CO ₃	11% CO ₂ /Ar, 1 min, 1200 ml min ⁻¹ , <i>T</i> = 400 °C 1 atm	10% H ₂ /Ar, 2 min, 1200 ml min ⁻¹ , <i>T</i> = 400 °C, 1 atm	0.42	94	0.39	>99		52
Ru ₁₀ CaO	Same as above	Same as above	0.34	80	0.27	>99		
10% Ni/CaO	10% CO ₂ + 10% H ₂ O + 80% N ₂ , 120 min, 40 ml min ⁻¹ , <i>T</i> = 500 °C, 1 atm	90% H ₂ /N ₂ , 230 min, 40 ml min ⁻¹ , <i>T</i> = 500 °C, 1 atm	8.96	93	8.34	93	5 cycles	43
10% Ni/CaO	10% CO ₂ + 10% H ₂ O + 80% N ₂ , 120 min, 40 ml min ⁻¹ , <i>T</i> = 600 °C, 1 atm	90% H ₂ /N ₂ , 230 min, 40 ml min ⁻¹ , <i>T</i> = 600 °C, 1 atm	15.49	96	14.94	96	NA	
10% Ni/CaO	10% CO ₂ + 10% H ₂ O + 80% N ₂ , 120 min, 40 ml min ⁻¹ , <i>T</i> = 700 °C, 1 atm	90% H ₂ /N ₂ , 230 min, 40 ml min ⁻¹ , <i>T</i> = 700 °C, 1 atm	16.22	83	4.7	29	NA	
15% Ni 15% CaO/Al ₂ O ₃	10% CO ₂ /Ar, 1 min, 1200 ml min ⁻¹ , <i>T</i> = 520 °C, 1 atm	10% H ₂ /Ar, 2 min, 1200 ml min ⁻¹ , <i>T</i> = 520 °C, 1 atm	0.16	88	0.14	87		41
15% Ni 15% Na ₂ CO ₃ /Al ₂ O ₃	10% CO ₂ /Ar, 1 min, 1200 ml min ⁻¹ , <i>T</i> = 400 °C, 1 atm	10% H ₂ /Ar, 2 min, 1200 ml min ⁻¹ , <i>T</i> = 400 °C, 1 atm	0.21	88	0.19	86		



Table 1 (Contd.)

DFMs	Adsorption process	Hydrogenation process	CO ₂ cap. ^a	CO ₂ con. ^b	CH ₄ yield ^c	CH ₄ sel. ^d	Cycle	Ref.
2D-layered Ni-MgO-Al ₂ O ₃ , 2.0NiMgAl-LDO-re	15% CO ₂ /N ₂ , 25 s, 70 ml min ⁻¹ , T = 250 °C, 1 atm	100% H ₂ , 35 s, 70 ml min ⁻¹ , T = 250 °C, 1 atm	0.32	100	NA	100	10 cycles	42
1% Ni/CeO ₂ -CaO-physically mixed	15% CO ₂ /N ₂ , 60 min, 50 ml min ⁻¹ , T = 550 °C, 1 atm	100% H ₂ , 60 min, 50 ml min ⁻¹ , T = 550 °C, 1 atm	15.3	62	8.0	84		53
5% Ru/CeO ₂ -MgO	65% CO ₂ /N ₂ , 60 min, 50 ml min ⁻¹ , T = 300 °C, 1 atm	5% H ₂ /N ₂ , 60 min, 50 ml min ⁻¹ , T = 300 °C, 1 atm	4.25	79	3.36	NA	10 cycles	54

^a CO₂ capture capacity (mmol g_{DFM}⁻¹). ^b CO₂ conversion (%). ^c CH₄ yield (mmol g_{DFM}⁻¹). ^d CH₄ selectivity (%).

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.*⁴¹ 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 capacity, CH₄ yield and CO yield. A similar trend of temperature related to CO₂ capture capacity was observed by Zhou *et al.*⁴² and Jo *et al.*⁴³ The matching of temperature between adsorption and methanation is also very important for ICCU. Generally, lower process temperature promotes CH₄ selectivity but decreases CO₂ conversion for ICCU-methanation. By comparing different temperatures (280–350 °C), Zheng *et al.*⁴⁴ achieved the best ICCU performance at 320 °C (32.41 ml CO₂ captured and 31.56 ml CH₄ generated). A higher temperature was found to decrease the CO₂ capture capacity and cause excessive oxidation of Ru for the processing of O₂-containing flue gas (32.86 ml CO₂ captured and 29.73 ml CH₄ generated at 350 °C), while a lower temperature significantly limited the catalytic activity (41.21 ml CO₂ captured and 1.2 ml CH₄ generated at 280 °C).

In addition to the effect of temperature, the reaction time of adsorption and conversion stages also affects the catalytic performance. Zheng *et al.*⁴⁴ investigated the influence of adsorption time on ICCU-methanation. Increasing the reaction time of adsorption benefited the generation of CH₄. However, it was found that the CO₂ adsorption rate dropped significantly after 20 min. In addition, a longer adsorption time resulted in the deactivation of catalysts by inducing excessive oxidation of catalysts in the flue gas. As listed in Table 1, most of the research used more than 20 min reaction time in the first carbon capture stage. This could increase the overall CO₂ capture capacity. However, it might not be beneficial to the overall ICCU-methanation process. Excessive CO₂ adsorption could produce more carbonates than active formate species which are mainly responsible for the formation of methane. For example, Zhou *et al.*⁴² applied a fast adsorption and methanation process (25 s and 35 s for adsorption and methanation) and

reported a nearly 100% CO₂ conversion. This was due to the formation of dominant formate species and few carbonates.

The concentration of H₂ is another important parameter that has a significant impact on CH₄ yield. Wang *et al.*⁴⁸ investigated the influence of H₂ partial pressure (5% and 10% H₂/N₂) and found that the presence of more sufficient H₂ could generate more CH₄ (58.66 ml and 131 ml CH₄). The authors reported that a higher H₂ concentration is important for the activation of Ru-based DFMs when processing O₂-containing flue gas. A higher H₂ concentration could also effectively improve the CO₂ conversion by positively promoting the equilibrium of CO₂ methanation.^{43,53} Apart from the gas concentration, GHSV also influences the ICCU performance by altering the gas diffusion pathways within DFMs.⁴⁴ Generally, a higher GHSV results in an enhanced CO₂ conversion and is accomplished with higher H₂ consumption.

In practice, it is known that contaminants in flue gas such as H₂O and O₂ can affect CO₂ capture⁵⁵ and conversion.⁵⁶ Martha *et al.*⁵⁰ simulated a flue gas by mixing 4.5% O₂ and 15% H₂O with 7.5% CO₂/N₂ to investigate CH₄ formation using Ni-based DFMs. The reduction of ICCU performance in relation to CH₄ 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.⁴⁴ Interestingly, the presence of H₂O might not always play a negative role in ICCU. Miguel *et al.*⁴⁷ 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.⁴⁷

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



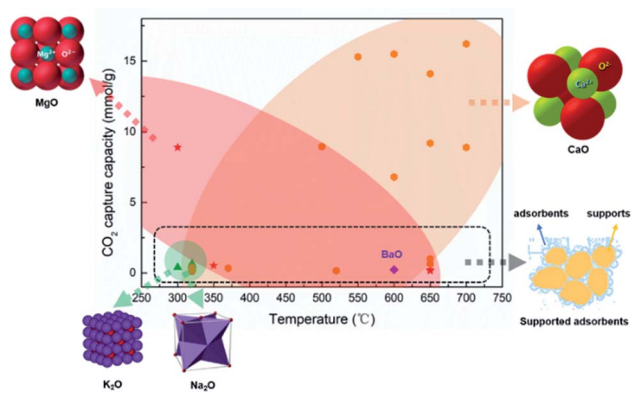


Fig. 2 Summary of the CO₂ adsorption capacity of DFMs applied in ICCU.^{41–54} (orange zone: CaO application in ICCU; red zone: MgO application in ICCU; green zone: K₂O and Na₂O application in ICCU; black dotted zone: supported adsorbent application in ICCU).

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 mmol_{CH₄} g_{DFM}^{−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.⁵⁷ 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.⁴⁸ 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 alkali metal (Li, Na, and K) promoted MgO in DFMs and obtained ~4 mmol

g_{DFM}^{−1} CO₂ capacity after 10 cycles at a temperature below 300 °C. Attractively, Zhou *et al.*⁴² 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.*⁴² observed the formation of formate species in the CO₂ capture process, which was formed from the hydrogenation 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.

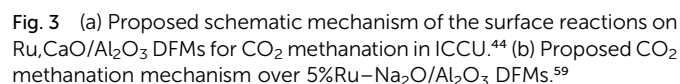
In addition, the carriers used to disperse the adsorbent affect the adsorption performance in ICCU-methanation. For example, Martha *et al.*⁵⁰ studied carrier materials, including CeO₂, CeO₂/ZrO₂, Nazeolite-X, H-mordenite zeolite, SiC, SiO₂ and ZrO₂–Y and demonstrated that γ -Al₂O₃ was the most suitable 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



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.*⁴⁵ applied 5 wt% Ru/CaO/ γ -Al₂O₃ DFMs in ICCU-methanation and obtained around 290 $\mu\text{mol g}_{\text{cat}}^{-1}$ CH₄ yield. Sun *et al.*⁵⁴ utilized 10 wt% Ru/CeO₂-MgO and achieved higher CH₄ yield (7.07 mmol $\text{g}_{\text{cat}}^{-1}$) and CO₂ conversion (89%) in ICCU-methanation. Ru-based DFMs have also shown excellent stable performance in ICCU. Wang *et al.*⁴⁹ applied 5% Ru-6.1% Na₂O/ γ -Al₂O₃ DFMs and obtained 0.35 mmol $\text{g}_{\text{cat}}^{-1}$ 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.*⁴⁴ investigated the performance of Ru-CaO/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.



The addition of additives could promote the catalytic performance of DFMs for ICCU-methanation. For example, Stefano *et al.*⁶² introduced various alkali metals (Li, Na, and K carbonates *vs.* nitrates) into 1% Ru/Al₂O₃ DFMs and found that

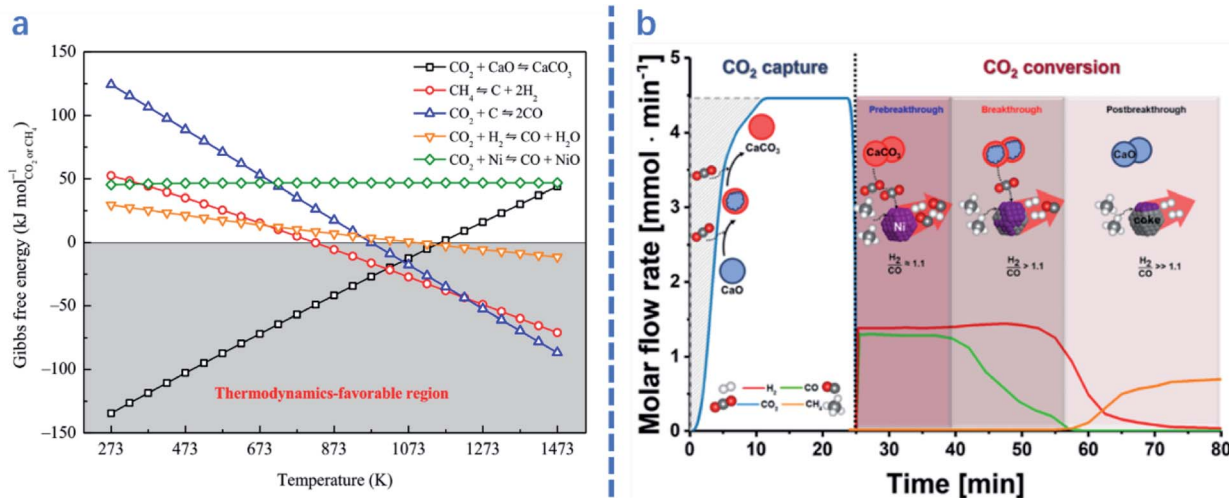
Integrated CO₂ capture and dry reforming (ICCU-DRM) provides a promising solution for utilizing low carbon alkanes accompanied by the reduction of CO₂ emissions. Synthesizing liquid fuels or high-value hydrocarbons by Fischer–Tropsch synthesis using the products from the ICCU-DRM process could be a practical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

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

3.1 Influence of process parameters on ICCU-DRM

Temperature is one of the most effective parameters to influence the balance of DRM and side reactions. Molina-Ramírez *et al.*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.*⁶⁷ investigated the influence of reaction temperature on Ni₂₀@(K–Ca)₅₀/(γ–Al₂O₃)₅₀ 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

Compared to CO_2 , the greenhouse effect of CH_4 is 22 times higher. Currently, CH_4 is widely used to produce H_2 by chemical looping reforming⁶³ or steam methane reforming.⁶⁴ Dry reforming of methane (DRM) utilizing these two major greenhouse gases, as shown in eqn (2), has received increasing attention in recent years.^{36,65} In addition to CH_4 , C_2H_6 and other low-carbon alkanes could also be used for dry reforming.



3.2.2. Catalysts in DFMs for ICCU-DRM. As DRM requires a large amount of energy to process owing to its thermodynamic properties,⁶⁸ 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.



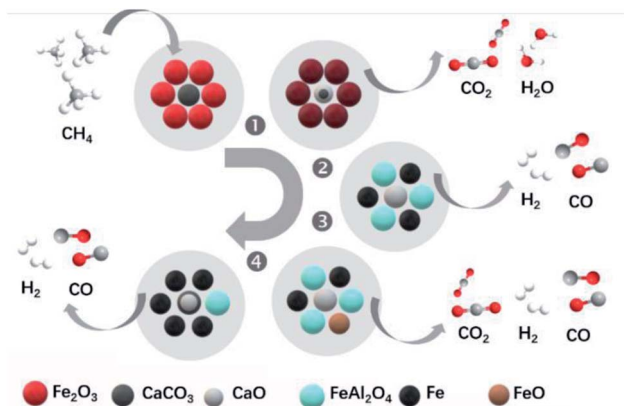
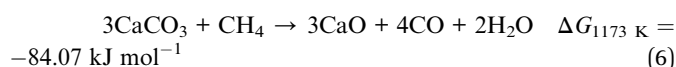
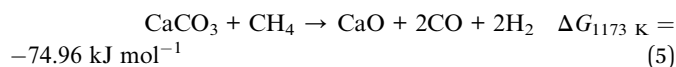
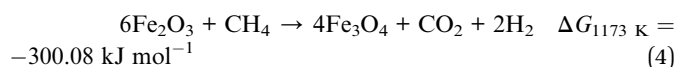
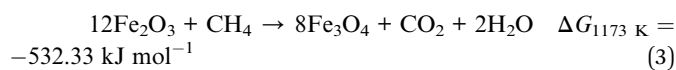


Fig. 6 Diagram of the reaction mechanism for the novel Ca-Fe chemical looping reforming process.³

Fe-based catalysts also showed a good performance for ICCU-DRM. For example, Zhao *et al.*³ 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. Fe₃O₄ was gradually transformed into Fe and FeAl₂O₄ 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.

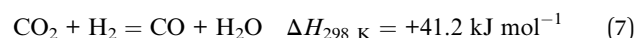


Introducing specific additives promotes ICCU-DRM. Ahmed *et al.*⁶⁷ proposed that a K-introduced DFM showed better reducibility than a Na-introduced DFM by enhancing catalyst-support interactions. The promotion effect of Ni-Ca

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.^{69,70} 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.



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.*⁷¹ reported that a higher temperature improved both CO₂ conversion and CO selectivity owing to the endothermic properties of

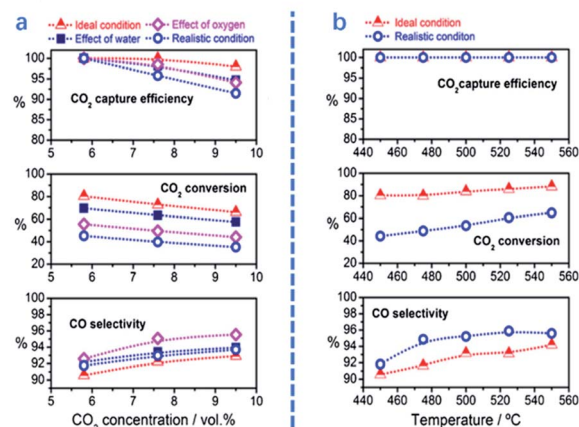


Fig. 7 CO₂ capture efficiency, CO₂ conversion, and CO selectivity as a function of (a) CO₂ concentration (5.8–9.5%) at 450 °C and (b) reaction temperature with 5.8% CO₂. The gas composition–capture phase: CO₂ diluted in nitrogen (ideal condition), CO₂ diluted in nitrogen saturated with 4% of water vapour (effect of water), CO₂ diluted in nitrogen with 4% of oxygen (effect of oxygen) and CO₂ diluted in nitrogen with 5% of oxygen and 4% of water (realistic condition). Gas hourly space velocity (GHSV)–1620 ml g_{cat}^{−1} h^{−1}. Reduction phase: Pure hydrogen with a GHSV of 3900 ml g_{cat}^{−1} h^{−1}. The CCR period length was 215 s, i.e. 107.5 s for the CO₂ capture and reduction phase.⁷¹

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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(LDO)/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, imidazolydene heterocyclic carbenes, and zeolitic imidazolate frameworks are also commonly used materials to realize this process.³³ 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 inertness of CO₂ molecules.¹²⁴ Therefore, many researchers developed various finely designed materials to improve the efficiency of CO₂ conversion. For example, Jiang *et al.*¹²⁴ 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.*¹²⁵ 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.*¹²⁸ 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 large-scale 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



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