

Cite this: *RSC Sustainability*, 2025, 3, 4457Received 2nd May 2025
Accepted 13th August 2025

DOI: 10.1039/d5su00317b

rsc.li/rscsus

Integrated carbon capture and dry reforming of methane of mechanochemically synthesised dual-function materials

Loukia-Pantzechroula Merkouri,^a Maila Danielis,^b Andrea Braga,^b Tomas Ramirez Reina,^c Alessandro Trovarelli,^b Sara Colussi^{b*} and Melis S. Duyar^{b*}

Herein we report a green mechanochemical synthesis with low energy input of dual-function materials for integrated CO₂ capture and dry reforming of methane. The materials produced syngas during the CH₄ step (up to 0.6 mmol g⁻¹ CO and 7.7 mmol g⁻¹ H₂) and CO during the CO₂ step (up to 3.1 mmol g⁻¹) via the reverse Boudouard reaction due to the carbon produced from CH₄ cracking.

Introduction

Nowadays, there is an urgent need to deal with the increased carbon dioxide (CO₂) emissions in order to achieve net-zero CO₂ emissions by 2050 according to the Paris Agreement.^{1,2} Atmospheric CO₂ has increased from ca. 270 ppm in the pre-industrial era to 426 ppm in July 2024 with 37.4 Gt of CO₂ emitted in 2023, reaching a record high.³⁻⁵ Another alarming greenhouse gas is methane (CH₄), which is 25 times more harmful than CO₂.⁶ In fact, its atmospheric concentration has increased from 715 ppb in the pre-industrial era to 1930 ppb in February 2024,^{5,6} and its emissions were 135 Mt in 2022, corresponding to ca. 4 Gt of CO₂ equivalent.⁷ As a way of combating the CO₂ emissions, Carbon Capture and Storage (CCS) and Carbon Capture and Utilisation (CCU) have extensively been studied because CO₂ can be captured and then either stored in the underground formations or used to form added-value fuels and chemicals.⁸⁻¹¹

One of the most promising CO₂ utilisation reactions is dry reforming of methane (DRM), during which CO₂ reacts with CH₄ and hence, syngas, *i.e.* a mixture of carbon monoxide (CO) and hydrogen (H₂), is obtained (eqn (1)).¹²⁻¹⁵ The stoichiometric H₂/CO ratio is 1, which is useful for the production of long chain hydrocarbons and oxygenated chemicals. However, the

Sustainability spotlight

Carbon capture, utilisation, and storage (CCUS) presents itself as a necessary part of the solution to achieve net-zero CO₂ emissions by 2050. CCU entails the capture of CO₂, its compression/transportation, and its conversion into fuels and chemicals. By integrating the capture and utilisation steps, more efficient technologies are developed with reduced cost and energy requirements. Therefore, we investigate a cyclic process with two greenhouse gases (CO₂-CH₄) being introduced to our system separately, producing synthesis gas (CO-H₂). We also propose a further sustainable advancement of the technology by using green, mechanochemical synthesis, where the elimination of solvents allows for energy and waste reduction. Our work aligns with the UN sustainable development goals of affordable and clean energy (Goal 7), responsible consumption and production industry (Goal 12), and climate action (Goal 13).

obtained ratio is typically below 1 during steady-state operation due to the simultaneous occurrence of the reverse water-gas shift (RWGS) reaction (eqn (2)).^{12,16,17} Possible side reactions apart from RWGS include CH₄ cracking (eqn (3)) and Boudouard reaction (eqn (4)), both resulting in catalyst deactivation due to carbon depositions.¹⁴ Typical catalysts for DRM include Ni, Co, and noble metals (*e.g.* Ru, Rh).¹⁸⁻²⁶



Recently, the integrated CO₂ capture and DRM (ICC-DRM) has been proposed as a CO₂ mitigation technology.^{27,28} By combining the CO₂ capture and DRM processes, two harmful greenhouse gases are utilised, and the overall process efficiency is increased because the compression and transportation of both CO₂ and CH₄ are eliminated.^{4,28,29} ICC-DRM involves the

^aSchool of Chemistry and Chemical Engineering, University of Surrey, Guildford GU2 7XH, UK. E-mail: m.duyar@surrey.ac.uk

^bDipartimento Politecnico, Università degli Studi di Udine, Via del Cotonificio 108, 33100 Udine, Italy. E-mail: sara.colussi@uniud.it

^cDepartment of Inorganic Chemistry and Materials Sciences Institute, University of Seville-CSIC, 41092 Seville, Spain



capture of CO₂ from a CO₂-containing stream, targeting CO₂ upgrading in a subsequent DRM reaction. ICC-DRM resembles the typical chemical looping reforming process, but their main difference is the employment of a CO₂-containing stream instead of air. As a result, there are various names for the same process in literature, such as ICC-DRM, chemical looping CH₄ conversion with separated CO₂ utilisation, and chemical (or calcium when Ca is used) looping/reforming and DRM.^{27,28,30}

In order for the ICC-DRM to work, the material selected needs to be able to both capture the CO₂ from a waste stream and convert it into syngas by using CH₄. This type of material is known as a dual-function material (DFM). DFMs consist of an adsorbent, such as calcium oxide (CaO) or sodium oxide (Na₂O), and a catalytic active phase, such as Ni, Ru, and Rh, which are co-dispersed onto a high surface support (*e.g.* Al₂O₃). To date, DFMs have been used for other reactions, such as the CO₂ methanation and RWGS,^{4,31–37} but their development in DRM is still in early stages.^{29,38–53}

Regarding the DFMs synthesis method, the most widely used is impregnation, followed by sol gel method.^{4,32–34,54–58} However, the solvent-free mechanochemical synthesis, where solid precursors are appropriately mixed in a ball-mill to generate the desired material,^{59–61} can be a more sustainable method than the currently employed wet-based ones because of the reduced solvent needs and faster preparation times (hours *vs.* days), resulting in decreased energy requirements (less thermal treatments required), waste generation (solvents), and costs.⁶⁰ These advantages stem from the removal of solvents from the synthesis procedure, and cover many of the suggested principles of green chemistry.⁶¹ The metallic dispersion is achieved by mechanical energy, bypassing the chemical and thermal equilibria involved in wet-based syntheses, producing dispersed metal catalysts that exhibit an improved performance in various reactions,^{61–67} including conventional DRM.^{26,68} In our previous work,⁶¹ we investigated the performance of mechanochemically synthesised DFMs for the first time. Those milled DFMs had Ni and Ru nanoparticles as the catalytic phase, either Na₂O or CaO as the adsorbent, and CeO₂–Al₂O₃ as the support, and they were tested in the CO₂ capture-RWGS process. The milling process resulted in improved dispersion of Ni, Ru and Ca when co-milled and calcined in a single step,⁶¹ surpassing conventionally prepared DFMs with comparable composition⁴¹ and, remarkably, despite an observed decrease in surface area. However, a distinct increase in H₂ reactivity was also observed, leading to a large amount of CO release during the CO₂ capture. Herein we exploit their higher reducibility observed in RWGS compared to wet-impregnated samples in the DRM reaction. This work is the first time that DFM materials were synthesised mechanochemically and were tested in the ICC-DRM process. By expanding on our previous work, we show that it is feasible to use milled DFMs in ICC-DRM, a more challenging process which allows the upgrading of two greenhouse gases.

Experimental

Materials synthesis

All the samples of this work were prepared by the dry milling method, as reported elsewhere,⁶¹ and their composition was

chosen so as to be comparable of that of wet impregnated samples.^{41,69} A Fritsch Pulverisette 23 Mini-mill was used with a 15 mL ZrO₂ jar and 1 ZrO₂ sphere (diameter: 15 mm, weight: 10 g). All the precursors were milled at 15 Hz for 20 min.^{61,70} The support used was a commercial CeO₂–Al₂O₃ support from Sasol (SCFa-160 Ce20 Puralox, 20% CeO₂). The adsorbent salt used was either Ca(NO₃)₂ or NaNO₃ (both from Sigma-Aldrich), in order to ensure thermal decomposition at 600 °C while also maintaining a fair comparison with the wet impregnated references,⁴¹ and the adsorbent loading was 10 wt% of the final DFM formulation. All the DFMs had 15 wt% Ni and 1 wt% Ru, and the precursors were either metallic nanopowders (Ru black from Strem Chemicals and Ni nanopowders from Sigma-Aldrich) or acetate salts (Ru(III) acetylacetonate and Ni acetate, both from Sigma-Aldrich). Indeed, for the active metals, metallic nanopowders and organic precursors showed the best properties in the milling synthesis,^{70,71} due to their non hygroscopic nature and minimum hardness compared to nitrates and metal oxides, respectively.^{72,73} In addition, better dispersion values could be achieved.^{71,72} We prepared nine (9) samples in total, which are shown in Table 1. First the support (CA) was co-milled with the adsorbent precursor, followed by a calcination at 600 °C for 1 h in static air, forming the supported adsorbents. After that, either the metallic nanopowders or acetate salts were milled with the supported adsorbents, and a second calcination step took place at 600 °C for 1 h. The calcination steps were carried out to remove the organic ligands and to obtain comparable materials as the wet-impregnated DFMs. Two (2) more DFMs were prepared with either Na₂O or CaO and a single calcination step after the acetate precursors had been added. Finally, a reference catalyst was synthesised by using the metallic nanopowders without any adsorbent. A flowchart summarising the synthesis process is reported in the SI (Fig. S1).

Activity tests in ICC-DRM

The cyclic CO₂ capture-DRM experiments of the milled samples were carried out in a tubular fixed bed quartz reactor (0.5 in OD), and the samples were placed on top of a quartz wool bed.^{41,61,74} The outlet gas stream was analysed by an ABB AO2020 online gas analyser, after it had passed through a H₂O condenser. The outlet volumetric percentages of CO₂, CO, CH₄, and H₂ were recorded every 5 s with the remaining percentage being attributed to N₂. The accurate measurement of the total outlet volumetric flow rate was achieved by a bubble meter. Since N₂ was used as an internal standard,^{41,74} its flow rate was not changed throughout the experiment (45 mL min⁻¹). Initially, 0.250 g of sample was reduced at 800 °C for 1 h (10 °C min⁻¹) by using 50 mL min⁻¹ of a 10% H₂/N₂ mixture. Then, the temperature was decreased to 650 °C in N₂, and 5 cycles of CO₂ capture-DRM took place. Each CO₂ step lasted 5 min, and each CH₄ step lasted 3 min. The total flow rate in both steps was 50 mL min⁻¹, and the gaseous mixtures used were either 10% CO₂/N₂ or 10% CH₄/N₂. A N₂ purge step was performed after each step to ensure zero readings of the gases, demonstrating that the produced gases were formed from the captured CO₂.



Table 1 List of samples and brief description of synthesis parameters

#	Sample	Catalyst precursor	Calcination step (temperature, time)	# of calcination steps	Milling parameters (frequency, time)	# of milling steps
1	RuNi(M)/CaO/CA	Metallic nanopowders	600 °C/1 h	2	15 Hz/20 min	2
2	RuNi(Ac)/CaO/CA	Acetate salts	600 °C/1 h	2	15 Hz/20 min	2
3	RuNi(Ac) + CaO/CA	Acetate salts	600 °C/1 h	1	15 Hz/20 min	1
4	RuNi(M)/Na ₂ O/CA	Metallic nanopowders	600 °C/1 h	2	15 Hz/20 min	2
5	RuNi(Ac)/Na ₂ O/CA	Acetate salts	600 °C/1 h	2	15 Hz/20 min	2
6	RuNi(Ac) + Na ₂ O/CA	Acetate salts	600 °C/1 h	1	15 Hz/20 min	1
7	CaO/CA	N/A	600 °C/1 h	1	15 Hz/20 min	1
8	Na ₂ O/CA	N/A	600 °C/1 h	1	15 Hz/20 min	1
9	RuNi(M)/CA	Metallic nanopowders	600 °C/1 h	1	15 Hz/20 min	1

The N₂ purge after the CO₂ step was 10 min, and the N₂ purge after the CH₄ step was 15 min. The duration of the N₂ purge steps was exactly the same for all the materials tested in this work.

It should be mentioned that the purpose of having a very short CH₄ step was to limit the CH₄ cracking reaction by attempting to pulse a small amount of CH₄, which was rendered impossible in the end due to our reactor setup and mass flow controllers. The DFMs were tested for only 5 cycles in order to avoid the rig running overnight. The following equations (eqn (5) and (6)) were used for the calculation of the carbon balance and the residual carbon, respectively. It should be noted that the amount of H₂ formed due to CH₄ cracking was calculated by subtracting the amount of H₂ formed due to the DRM reaction (by assuming it was equal to the amount of CO, eqn (4)) from the total amount of H₂ formed in the CH₄ step.

Carbon balance :

$$100 \times \frac{\text{CO formed in the subsequent CO}_2 \text{ capture step}}{\text{H}_2 \text{ formed in the CH}_4 \text{ step from CH}_4 \text{ cracking}} \quad (5)$$

Residual carbon :

$$\begin{aligned} & \text{C from CH}_4 \text{ cracking} - \text{C from reverse Boudouard} \\ &= \frac{1}{2} \times \text{H}_2 \text{ formed in the CH}_4 \text{ step from CH}_4 \text{ cracking} \quad (6) \\ & - \frac{1}{2} \times \text{CO formed in the subsequent CO}_2 \text{ capture step} \end{aligned}$$

The post activity test samples were characterised by XRD. An X'Pert Powder apparatus from PANalytical was used, and the diffraction patterns were collected at 30 mA and 40 kV by using Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) while the 2θ angle was increased every 450 s by 0.05° in the range of 10–90°. The average Ni crystalline size was estimated by the Scherrer's equation at 44.5° (Ni(111) phase).

Results and discussion

The performance of all samples, *i.e.* the DFMs, the supported adsorbents, and the catalyst, was evaluated in ICC-DRM. Fig. 1 shows the quantities of products, CO and H₂, and the H₂/CO ratio during the CH₄ steps. A comparison with similar samples

prepared by conventional methods is reported in Table S1. By observing Fig. 1a, it was made clear that all 9 samples, including the supported adsorbents and the catalyst, were active in ICC-DRM. That meant that they were able to capture the CO₂ during the CO₂ steps and then convert it into syngas *via* the DRM reaction. The most active sample was by far sample 3 (RuNi(Ac) + CaO/CA), which produced 588 $\mu\text{mol g}^{-1}$ of CO on average during the CH₄ steps. This sample achieved a high degree of interaction between the DFM components and a good dispersion of both the catalyst and the adsorbent through the dry milling of Ca with the acetate precursors, followed by a single calcination step, as characterised *via* scanning transmission electron microscopy results in our previous publication.⁶⁴ The amount of CO formed during the CH₄ steps seemed to be fairly stable over the cycles for all samples, and the order of DFMs according to their average CO production in CH₄ steps was: sample 3 (588 $\mu\text{mol g}^{-1}$) > sample 1 (295 $\mu\text{mol g}^{-1}$) > sample 2 (257 $\mu\text{mol g}^{-1}$) > sample 5 (200 $\mu\text{mol g}^{-1}$) > sample 6 (194 $\mu\text{mol g}^{-1}$) > sample 9 (181 $\mu\text{mol g}^{-1}$) > sample 4 (174 $\mu\text{mol g}^{-1}$) > sample 7 (67 $\mu\text{mol g}^{-1}$) > sample 8 (62 $\mu\text{mol g}^{-1}$).

Fig. 1b displays the amount of H₂ produced during the CH₄ steps, which was much higher than the amount of CO for all samples. From Fig. 1c, it was clear that the H₂/CO was much higher than the stoichiometric value, with the highest H₂/CO observed for sample 2, *i.e.* 21.3. This indicated that a side reaction took place, namely the CH₄ cracking reaction (eqn (3)). Once the adsorbed CO₂ had been consumed, the high temperature used in these experiments (650 °C) allowed the endothermic CH₄ cracking reaction to take place, producing an excess amount of H₂. Interestingly, the amount of H₂ produced decreased over the cycles except for the supported adsorbents (samples 7 and 8). That indicated that the extent of CH₄ cracking was reduced over time, meaning that the surface of DFMs was not 'clean' of carbon depositions, which in turn hindered the CH₄ cracking reaction over the cycles. The order of samples according to their average H₂ production in CH₄ steps was: sample 3 (7697 $\mu\text{mol g}^{-1}$) > sample 2 (5504 $\mu\text{mol g}^{-1}$) > sample 5 (3455 $\mu\text{mol g}^{-1}$) > sample 6 (3042 $\mu\text{mol g}^{-1}$) > sample 1 (2773 $\mu\text{mol g}^{-1}$) > sample 9 (2677 $\mu\text{mol g}^{-1}$) > sample 4 (1847 $\mu\text{mol g}^{-1}$) > sample 7 (798 $\mu\text{mol g}^{-1}$) > sample 8 (776 $\mu\text{mol g}^{-1}$). This order was the same as the order of the CO production with the only difference being sample 1, which dropped to the 5th place, explaining why it had the lowest H₂/CO in Fig. 1c.





Fig. 1 Amount of (a) CO and (b) H₂ formed, and corresponding (c) H₂/CO ratio measured during the CH₄ steps. (1) RuNi(M)/CaO/CA; (2) RuNi(Ac)/CaO/CA; (3) RuNi(Ac) + CaO/CA; (4) RuNi(M)/Na₂O/CA; (5) RuNi(Ac)/Na₂O/CA; (6) RuNi(Ac) + Na₂O/CA; (7) CaO/CA; (8) Na₂O/CA; (9) RuNi(M)/CA. The red dashed square indicates the best performing samples.

Overall, the Ca-containing DFMs exhibited the best ICC-DRM performance, which was expected because Ca is more efficient in capturing CO₂ at higher temperatures than Na due to its higher amount of medium-strong basic sites.^{41,75,76} In our case, Ca was expected to have formed more stable carbonates compared with Na and so, less amount of weakly CO₂ was desorbed during the N₂ purge steps, leading to higher reforming efficiency.^{28,34,75–79} The supported adsorbents had the worst performance because they did not have Ni or Ru in their formulation to boost the conversion of the adsorbed CO₂ into syngas. After all, Ni and Ru are perhaps the most active and widely used metals for the DRM reaction.^{12–15,80,81} In contrast, the opposite trend was observed during their CO₂ capture-RWGS experiments⁶¹ as the supported adsorbents were the most active samples after sample 3, suggesting that RWGS mainly took place due to the adsorbent and/or CeO₂. In the ICC-DRM case, the supported adsorbents did produce some amounts of CO and H₂ because of the adsorbent itself and the ability of CeO₂ to help catalyse the DRM reaction,^{21,82–86} but not as large CO and H₂ quantities as the DFMs due to the lack of the active metal phase. The reference catalyst was also able to produce syngas. Ni and Ru had the ability to adsorb CO₂ and form carbonyl species, which were converted into CO and H₂

during the CH₄ steps.^{87–92} In fact, the amount of CO produced by the catalyst was similar to the amount of CO produced by the Na-containing DFMs, while the catalyst (sample 9) outperformed sample 4 in both CO and H₂ production too. By comparing sample 1 (RuNi(M)/CaO/CA), sample 4 (RuNi(M)/Na₂O/CA), and sample 9 (RuNi(M)/CA), it was deduced that only the Ca adsorbent enhanced the ICC-DRM performance and so, Na was not a good adsorbent at the selected temperature (650 °C).⁷⁹ Hence, a synergy between the Ca adsorbent, support, and NiRu is necessary for successful ICC-DRM applications, where Ca efficiently binds CO₂⁷⁶ which is then made available to close Ni and Ru sites⁶¹ for CH₄ reforming to syngas. Opposite trends regarding the number of calcination steps were observed for the two sorbent elements. As regards the Na-containing DFMs, sample 5 (2 calcination steps) was marginally more active than sample 6 (1 calcination step). On the other hand, regarding the Ca-containing DFMs, sample 3 (1 calcination step) was more active than sample 2 (2 calcinations steps), likely due to the improved Ca–Ni–Ru proximity induced by the milling synthesis.⁶¹

By comparing the type of precursor used, the acetate precursor (sample 5) was better than the metallic nanopowders (sample 4) when Na was used as an adsorbent. The results



varied for the Ca-containing DFMs (samples 1 and 2). Even though sample 1 (RuNi(M)/CaO/CA) produced more CO than sample 2 (RuNi(Ac)/CaO/CA), the opposite was true for the H₂ production. It clearly showed that sample 2 was more susceptible to CH₄ cracking reaction compared to sample 1, as seen in Fig. 1c.

Fig. 2 illustrates the CO and H₂ volumetric flow rates of the most active Ca-containing (sample 3) and Na-containing (sample 5) samples, and the remaining samples are shown in Fig. S2. Both samples produced a much larger amount of H₂ than CO during the CH₄ steps, as Fig. 1 showed. It seemed that the DFMs produced a high quantity of H₂ during the CH₄ steps and a high quantity of CO during the CO₂ steps, apart from the first CO₂ step. The small amount of CO during the first CO₂ step was attributed to the occurrence of the RWGS reaction between the available CO₂ and the chemisorbed H₂.^{41,61} It was also considered possible that the CO production happened because of CO₂ dissociation on highly reduced Ru, Ni, and CeO₂ sites.⁶¹ Larger amounts of CO were formed during the first CO₂ step of the Ca-containing DFMs (samples 1–3) compared to the Na-containing DFMs (samples 4–6) with an average CO production of 95 and 32 μmol g⁻¹, respectively, as Fig. S2 illustrates. Interestingly, the supported adsorbents and the catalyst (samples 7–9) produced a small amount of CO, *ca.* 11 μmol g⁻¹, indicating that Ce³⁺ was oxidised by CO₂, forming CO and Ce⁴⁺ and confirming our CO₂ dissociation hypothesis stated earlier. Ceria is well-known for its excellent redox properties, its increased oxygen vacancies, and its ability to catalyse the RWGS reaction.^{93–98} The formation of CO due to the decomposition of formate species (HCOO⁻) into CO and OH was not considered in this case, because DRIFTS studies of the corresponding wet-impregnated samples did not show the formation of formate species.^{87,88} Future DRIFTS experiments can be carried out to investigate the reaction mechanism of those DFMs, but those experiments are out of the scope of this work. Additionally, some amounts of H₂ were observed in every CO₂ capture step, indicating that H₂ was chemisorbed on the surface due to the

initial DFM reduction or CH₄ cracking and that it was then released upon a CO₂ flow.

The significant amounts of CO produced in the CO₂ steps indicated the gasification of carbon through the reverse Boudouard reaction (reverse eqn (4)). In effect, CO₂ reacted with the carbon formed in the preceding CH₄ step, producing substantial amounts of CO. Despite the production of excess H₂ in the CH₄ steps, it was observed that the onset of CO was at the same time as H₂, or perhaps few seconds before that, and that CO had stopped being produced after the first 5 min. In other words, DRM took place before CH₄ cracking, and as the time went by and the availability of adsorbed CO₂ decreased, CH₄ cracking became the dominant reaction. Even though the CH₄ flow lasted only 3 min, it took a considerable amount of time to purge the leftover CH₄ of the lines, and as long as CH₄ was still present, it continued to decompose into carbon and H₂. That meant that even though the CH₄ step lasted only 3 min and no CH₄ flowed after that time, CH₄ cracking continued to occur during the subsequent N₂ purge step, and it finished when there was no CH₄ left in the lines. Since H₂ was present in the CH₄ step, the simultaneous occurrence of RWGS during the CH₄ steps could not be ruled out completely since those DFMs have shown to be active in that reaction.⁶¹ It should be noted that CO₂ was not desorbed during the CH₄ steps in any of the samples apart from the most active sample (sample 3). However, its amount was so small (<<10 μmol g⁻¹) that could not be accurately quantified and so, it was concluded that DRM was a fast reaction and that all the adsorbed CO₂ had been converted into syngas.

Fig. 3 shows the amount of CO formed during the CO₂ steps and the residual amount of carbon left on the surface after each CO₂ step. Since the first step after the reduction of the DFMs was a CO₂ capture step and CH₄ had not been introduced to the reactor beforehand, there was only a very small amount of CO formed during the first CO₂ capture step. In addition, Fig. 3a reveals that the supported adsorbents produced minimal amounts of CO through the reverse Boudouard reaction and so, this reaction occurred due to the presence of Ni and Ru. Similar



Fig. 2 Volumetric flow rate of CO and H₂ vs. time graphs of the best performing (a) Ca-containing DFM (sample 3: RuNi(Ac) + CaO/CA) and (b) Na-containing DFM (sample 5: RuNi(Ac)/Na₂O/CA).



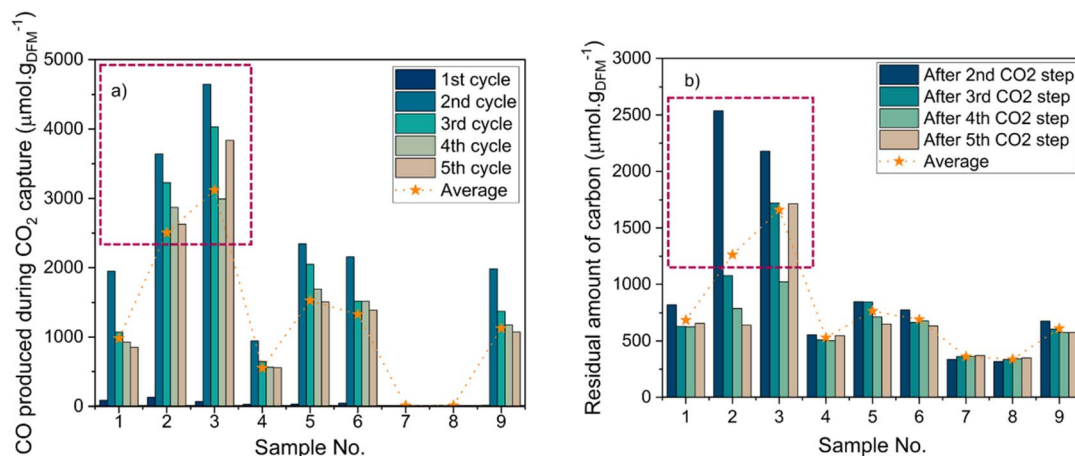


Fig. 3 (a) Amount of CO formed during the CO₂ steps and (b) amount of residual carbon (found by subtracting the carbon gasified in the subsequent CO₂ capture step from the carbon formed due to CH₄ cracking in the previous cycle). (1) RuNi(M)/CaO/CA; (2) RuNi(Ac)/CaO/CA; (3) RuNi(Ac) + CaO/CA; (4) RuNi(M)/Na₂O/CA; (5) RuNi(Ac)/Na₂O/CA; (6) RuNi(Ac) + Na₂O/CA; (7) CaO/CA; (8) Na₂O/CA; (9) RuNi(M)/CA. The red dashed square indicates the best performing samples.

to the amount of H₂ formed during the CH₄ steps (Fig. 1b), the amount of CO during the CO₂ steps decreased over the cycles, meaning that the extent of CH₄ cracking decreased over time. The order of samples based on the average amount of CO produced during the CO₂ steps was: sample 3 (3116 μmol g⁻¹) > sample 2 (2499 μmol g⁻¹) > sample 5 (1523 μmol g⁻¹) > sample 6 (1325 μmol g⁻¹) > sample 9 (1122 μmol g⁻¹) > sample 1 (976 μmol g⁻¹) > sample 4 (547 μmol g⁻¹) > sample 7 (4 μmol g⁻¹) > sample 8 (4 μmol g⁻¹). That order was the same as the H₂ production order with the only difference being the change of order between samples 1 and 9.

As both the production of H₂ from CH₄ cracking and CO from reverse Boudouard decreased over time, the amount of residual carbon remained somewhat stable (samples 1, 4, 7 and 8) or decreased over time (samples 2, 3, 5, 6 and 9), as illustrated in Fig. 3b. Based on Table S2, the carbon balance was not closed in any of the samples, likely due to a continuous accumulation of the carbon species from CH₄ cracking. Despite the gasification of carbon in the subsequent CO₂ capture step, it was not enough to get rid of the carbon completely. Apparently, the most active samples in ICC-DRM had the highest amount of residual carbon left. Since the amount of CO formed during the CH₄ steps (Fig. 1a) was stable over time, it was shown that the carbon accumulation did not affect the DRM activity of the designed DFMs. This was a significant result, but experiments with a duration of few days will be necessary in the future to observe their behaviour over longer periods of time. Carbon deposition, *i.e.* coking, is usually a well-known deactivation mechanism. The possibility of gasifying the carbon *via* the reverse Boudouard reaction, as demonstrated in this work, creates new opportunities for materials regeneration. Further material optimisation, for example by reducing Ni loading,⁹⁹ can also be explored to limit CH₄ cracking and the consequent carbon deposition. The DFM that had the most-closed carbon balance was sample 2 with an average carbon balance of 58%, followed by sample 5 (55%), samples 3 and 6 (54%), sample 1

(45%), and sample 4 (39%). This trend confirmed that the DFMs synthesised with acetate precursors were better than the ones with metallic nanopowders (Fig. 1). It is worth mentioning that the accurate quantification of carbon deposition by characterising the post samples was not feasible in this case. That was due to the complexity of the designed materials and the interference of carbonate decomposition, material oxidation, RuO_x volatility, and chemisorbed/adsorbed species (*e.g.* H₂O) with the carbon deposition analysis.

Fig. S3 and Table S3 show the post XRD patterns and estimated Ni particle sizes based on the Scherrer equation. The post XRD patterns were very similar to their *ex situ* reduced pattern, observed in our previous work.⁶¹ All samples presented the characteristic peaks of CeO₂ and γ-Al₂O₃ (JCPDS 03-065-5923 and JCPDS 00-004-0880, respectively). The DFMs also had metallic Ni peaks (JCPDS 01-070-1849). None of the samples showed any phase of Ru or the adsorbent (Ca/Na), meaning that those species were highly dispersed and/or amorphous. Despite the last step being a CH₄ step, no crystalline carbon peak was observed and so, the accumulated carbon was not graphitic, but soft/amorphous, facilitating possible regeneration pathways. Based on Table S3, the average crystalline size of Ni increased by 1–2 nm in the Na-containing DFMs (samples 4–6) and reference catalyst (sample 9) compared to their corresponding reduced samples. In the case of the Ca-containing DFMs (samples 1–3), it increased by *ca.* 5 nm. It could be concluded that the Ca-containing DFMs were more prone to sintering than the Na-containing DFMs. Since they were also the most active samples in the ICC-DRM, it was demonstrated that the formation of carbon depositions enhanced the metallic sintering to some extent in fair agreement with previous reports.^{100,101} However, the increase was not that significant, and the main culprit in our materials for the ICC-DRM process remained the carbon formation and accumulation, making necessary the implementation of a regeneration process and/or an optimisation of the DFM to suppress CH₄ cracking.



Conclusions

In this work, we used mechanochemically milled DFMs for the first time in ICC-DRM, demonstrating the feasibility of the dry milling synthesis method for this process. The six (6) milled DFMs investigated herein differed in the adsorbent (Na or Ca), the type of catalyst precursor (metallic nanopowders or acetate), and the number of calcination steps (1 or 2). The most active DFM was sample 3 that had Ca as an adsorbent and was synthesised by using acetate precursors and a single calcination step. In general, using Ca as an adsorbent and acetates as a catalyst precursor resulted in the best materials, due to the high temperature favouring calcium carbonates formation and the ease of dispersion allowed by Ni and Ru acetates. However, all samples tested, including the two supported adsorbents and the reference catalyst, produced CO and excess amounts of H₂ during the CH₄ steps, leading to a H₂/CO of more than 10. Even though DRM took place between the captured CO₂ and the available CH₄, significant quantities of H₂ were produced due to CH₄ cracking. As a result, carbon was formed and accumulated over time, only partially gasified in the subsequent CO₂ capture step through the reverse Boudouard reaction, releasing large amounts of CO. However, none of the samples had a closed carbon balance. Despite the carbon formation, the activity of DFMs in DRM was steady over the five cycles, allowing us to preliminarily validate the implementation of multicomponent DFMs systems prepared by milling for ICC-DRM as a smart strategy for chemical CO₂ recycling. The use of a solvent-free synthesis method has distinct advantages in terms of materials costs and waste reduction, directly correlated with the solvent use reduction, a consequent decrease in thermal treatment requirements, hence leading to energy and time savings. Additionally, a more facile scalability of this technology can be envisioned compared to other methods, such as sol-gel or combustion syntheses, since large-scale milling is already employed in other industrial processes while the sol-gel and combustion alternatives are difficult to reproduce and represent a safety problem at industry level. Another advantage of the milling method is the facilitation of fast material screening, that can be exploited for example to investigate the optimal Ni loading to balance high DRM activity with low CH₄ cracking and, consequently, low carbon deposition. Thus, a sample with optimal Ni loading might not require complex regeneration protocols, overcoming the issues observed so far. Nevertheless, further optimisation studies will likely be needed in the future aiming to minimise the carbon formation; this should include fine-tuning the DFMs composition (*e.g.* reducing metal content) and process conditions (*e.g.* reaction temperature and duration) as well as engineering a viable regeneration protocol (*e.g.* by using either hydrogen or air) to unlock the potential of DFMs for realistic ICC-DRM applications.

Author contributions

Loukia-Pantzechroula Merkouri: methodology, investigation, formal analysis, visualisation, writing – original draft. Maila Danilidis: methodology, investigation, formal analysis, writing – review

and editing. Andrea Braga: investigation, formal analysis, writing – review and editing. Tomas Ramirez Reina: formal analysis, writing – review and editing. Alessandro Trovarelli: supervision, resources. Sara Colussi: conceptualisation, writing – review and editing, supervision, resources. Melis S. Duyar: conceptualisation, formal analysis, writing – review and editing, supervision, funding acquisition, resources, project administration.

Conflicts of interest

There are no conflicts to declare.

Data availability

Data supporting this article have been included as part of the SI.

Supplementary information including details of material synthesis, further characterization and time dependent data from DFM activity tests. See DOI: <https://doi.org/10.1039/d5su00317b>.

Acknowledgements

This study was carried out within the Interconnected Nord-Est Innovation Ecosystem (iNEST) and received funding from the European Union Next-GenerationEU (PIANO NAZIONALE DI RIPRESA E RESILIENZA (PNRR) – MISSIONE 4 COMPONENTE 2, INVESTIMENTO 1.5 – D.D. 1058 23/06/2022, ECS00000043, CUP: G23C22001130006). M. D. is grateful for funding under the REACT EU Italian PON 2014–2020 Program – Action IV.4 – Innovation (DM 1062, 10/08/2021, CUP G51B21006040007). S. C., M. S. D. and T. R. R. acknowledge funding by the European Commission under the framework of C-NET project, HORIZON-MSCA-2023-SE-01, project reference: 101182598. M. S. D. acknowledges support by the Engineering and Physical Sciences Research Council (EPSRC) grant EP/X000753/1. Views and opinions expressed are however those of the author(s) only and do not necessarily reflect those of the European Union. Neither the European Union nor the granting authority can be held responsible for them. The team of the University of Surrey acknowledge the financial support for this work from the School of Chemistry and Chemical Engineering and the Doctoral College of the University of Surrey. SASOL is kindly acknowledged for providing the CeAl support.

References

- 1 United Nations Framework Convention on Climate Change, *Adoption of the Paris Agreement*, Paris, 2015.
- 2 J. Rogelj, M. Den Elzen, N. Höhne, T. Fransen, H. Fekete, H. Winkler, R. Schaeffer, F. Sha, K. Riahi and M. Meinshausen, *Nature*, 2016, **534**, 631–639.
- 3 *CO₂ Emissions in 2023*, <https://www.iea.org/reports/co2-emissions-in-2023>, accessed 16 September 2024.
- 4 L. P. Merkouri, T. R. Reina and M. S. Duyar, *Energy Fuels*, 2021, **35**, 19859–19880.
- 5 Global Surface Temperature|NASA Global Climate Change, *Climate Change: Vital Signs of the Planet*, <https://>



- climate.nasa.gov/vital-signs/carbon-dioxide/, accessed 16 September 2024.
- 6 O. Boucher, P. Friedlingstein, B. Collins and K. P. Shine, *Environ. Res. Lett.*, 2009, **4**, 044007.
 - 7 *CO₂ Emissions in 2022*, <https://www.iea.org/reports/co2-emissions-in-2022>, accessed 15 March 2023.
 - 8 J. C. M. Pires, F. G. Martins, M. C. M. Alvim-Ferraz and M. Simões, *Chem. Eng. Res. Des.*, 2011, **89**, 1446–1460.
 - 9 A. Al-Mamoori, A. Krishnamurthy, A. A. Rownaghi and F. Rezaei, *Energy Technol.*, 2017, **5**, 834–849.
 - 10 E. A. Quadrelli, G. Centi, J. L. Duplan and S. Perathoner, *ChemSusChem*, 2011, **4**, 1194–1215.
 - 11 J. Gibbins and H. Chalmers, *Energy Policy*, 2008, **36**, 4317–4322.
 - 12 E. le Saché and T. R. Reina, *Prog. Energy Combust. Sci.*, 2022, **89**, 100970.
 - 13 B. Abdullah, N. A. Abd Ghani and D. V. N. Vo, *J. Cleaner Prod.*, 2017, **162**, 170–185.
 - 14 S. Arora and R. Prasad, *RSC Adv.*, 2016, **6**, 108668–108688.
 - 15 J. M. Lavoie, *Front. Chem.*, 2014, **2**, 1–17.
 - 16 M. Usman, W. M. A. Wan Daud and H. F. Abbas, *Renewable Sustainable Energy Rev.*, 2015, **45**, 710–744.
 - 17 F. M. Baena-Moreno, M. Rodríguez-Galán, F. Vega, B. Alonso-Fariñas, L. F. Vilches Arenas and B. Navarrete, *Energy Sources, Part A*, 2019, **41**, 1403–1433.
 - 18 J. L. Martín-Espejo, L.-P. Merkouri, J. Gándara-loe, J. A. Odriozola, T. Ramirez Reina and L. Pastor-Pérez, *J. Environ. Sci.*, 2024, **140**, 12–23.
 - 19 J. L. Martín-Espejo, L. P. Merkouri, J. A. Odriozola, T. Ramirez Reina and L. Pastor-Pérez, *Ceram. Int.*, 2024, **50**, 38406–38414.
 - 20 S. A. Ali, M. Sa, L.-P. Merkouri, S. Soodi, A. Iakovidis, M. S. Duyar, D. Neagu, T. R. Reina and K. Kousi, *Front. Energy Res.*, 2023, **11**, 1–9.
 - 21 C. A. H. Price, W. Arnold, L. Pastor-Pérez, B. Amini-Horri and T. R. Reina, *Top. Catal.*, 2020, **63**, 281–293.
 - 22 E. le Saché, L. Pastor-Pérez, D. Watson, A. Sepúlveda-Escribano and T. R. Reina, *Appl. Catal., B*, 2018, **236**, 458–465.
 - 23 C. A. H. Price, L. Pastor-Pérez, T. Ramirez Reina and J. Liu, *React. Chem. Eng.*, 2018, **3**, 433–436.
 - 24 A. Álvarez Moreno, T. Ramirez-Reina, S. Ivanova, A. C. Roger, M. Á. Centeno and J. A. Odriozola, *Front. Chem.*, 2021, **9**, 1–10.
 - 25 I. Luisetto, S. Tuti, C. Baticchio, S. Lo Mastro and A. Sodo, *Appl. Catal., A*, 2015, **500**, 12–22.
 - 26 M. Armengol-Profítos, A. Braga, L. Pascua-Solé, I. Lucentini, X. Garcia, L. Soler, X. Vendrell, I. Serrano, I. J. Villar-Garcia, V. Pérez-Dieste, C. Escudero, N. J. Divins and J. Llorca, *Appl. Catal., B*, 2024, **345**, 123624.
 - 27 E. Wang, Z. Zhu, R. Li, J. Wu, K. Ma and J. Zhang, *Chem. Eng. J.*, 2024, **482**, 148476.
 - 28 A. Bhaskaran, S. A. Singh, B. M. Reddy and S. Roy, *Langmuir*, 2024, **40**, 14766–14778.
 - 29 J. Hu, P. Hongmanorom, V. V. Galvita, Z. Li and S. Kawi, *Appl. Catal., B*, 2021, **284**, 119734.
 - 30 Z. Zhou, Z. Sun and L. Duan, *Curr. Opin. Green Sustainable Chem.*, 2023, **39**, 100721.
 - 31 A. Tsiotsias, N. Charisiou, I. Yentekakis and M. Goula, *Chem. Proc.*, 2020, **2**, 35.
 - 32 J. Chen, Y. Xu, P. Liao, H. Wang and H. Zhou, *Carbon Capture Sci. Technol.*, 2022, **4**, 100052.
 - 33 K. Zhang, D. Guo, X. Wang, Y. Qin, L. Hu and Y. Zhang, *J. CO₂ Util.*, 2023, **72**, 102493.
 - 34 L.-P. Merkouri, A. I. Paksoy, T. R. Reina and M. S. Duyar, *ACS Catal.*, 2023, **13**, 7230–7242.
 - 35 A. I. Tsiotsias, E. Harkou, N. D. Charisiou, V. Sebastian, D. R. Naikwadi, B. van der Linden, A. Bansode, D. Stoian, G. Manos, A. Constantinou and M. A. Goula, *J. Energy Chem.*, 2025, **102**, 309–328.
 - 36 A. I. Tsiotsias, N. D. Charisiou, A. G. S. Hussien, V. Sebastian, K. Polychronopoulou and M. A. Goula, *Chem. Eng. J.*, 2024, **491**, 151962.
 - 37 A. I. Tsiotsias, N. D. Charisiou, A. G. S. Hussien, A. A. Dabbawala, V. Sebastian, K. Polychronopoulou and M. Goula, *J. Environ. Chem. Eng.*, 2024, **12**, 112712.
 - 38 S. Jo, J. H. Lee, J. H. Woo, T.-Y. Kim, H.-J. Ryu, B. Hwang, J. C. Kim, S. C. Lee and K. L. Gilliard-AbdulAziz, *Sustainable Energy Fuels*, 2022, **6**, 81–88.
 - 39 M. Najimu, S. Jo and K. L. Gilliard-AbdulAziz, *Acc. Chem. Res.*, 2023, **56**, 3132–3141.
 - 40 S. Jo, J. H. Woo, J. H. Lee, T. Y. Kim, H. I. Kang, S. C. Lee and J. C. Kim, *Sustainable Energy Fuels*, 2020, **4**, 5543–5549.
 - 41 L.-P. Merkouri, R. Reina and M. S. Duyar, *Nanoscale*, 2022, **14**, 12620–12637.
 - 42 S. Sun, Y. Zhang, C. Li, Y. Wang, C. Zhang, X. Zhao, H. Sun and C. Wu, *Sep. Purif. Technol.*, 2023, **308**, 122956.
 - 43 X. Zhao, S. Sun, Y. Zhang, Y. Wang, Y. Zhu, P. Williams, S. Guan and C. Wu, *Sep. Purif. Technol.*, 2023, **326**, 124866.
 - 44 S. Sun, C. Zhang, Y. Wang, X. Zhao, H. Sun and C. Wu, *Chem. Eng. J.*, 2023, **468**, 143712.
 - 45 S. Sun, Y. Wang, Y. Xu, H. Sun, X. Zhao, Y. Zhang, X. Yang, X. Bie, M. Wu, C. Zhang, Y. Zhu, Y. Xu, H. Zhou and C. Wu, *Appl. Catal., B*, 2024, **348**, 123838.
 - 46 L. Zhu, Z. Lv, X. Huang, S. Lu, J. Ran and C. Qin, *Fuel Process. Technol.*, 2023, **248**, 107838.
 - 47 S. Jo and K. L. Gilliard-AbdulAziz, *Small*, 2024, e2401156.
 - 48 S. M. Kim, P. M. Abdala, M. Broda, D. Hosseini, C. Copéret and C. Müller, *ACS Catal.*, 2018, **8**, 2815–2823.
 - 49 S. Tian, F. Yan, Z. Zhang and J. Jiang, *Sci. Adv.*, 2019, **5**, eaav5077.
 - 50 H. Gu, Y. Gao, S. Iftikhar and F. Li, *J. Mater. Chem. A*, 2022, **10**, 3077–3085.
 - 51 R. Han, S. Xing, Y. Wang, L. Wei, Z. Li, C. Yang, C. Song and Q. Liu, *Sep. Purif. Technol.*, 2023, **307**, 122808.
 - 52 B. Shao, Z. Q. Wang, X. Q. Gong, H. Liu, F. Qian, P. Hu and J. Hu, *Nat. Commun.*, 2023, **14**, 996.
 - 53 D. Pinto, L. Hu and A. Urakawa, *Chem. Eng. J.*, 2023, **474**, 145641.
 - 54 I. S. Omodolor, H. O. Otor, J. A. Andonegui, B. J. Allen and A. C. Alba-Rubio, *Ind. Eng. Chem. Res.*, 2020, **59**, 17612–17631.



- 55 S. Sun, H. Sun, P. T. Williams and C. Wu, *Sustainable Energy Fuels*, 2021, **5**, 4546–4559.
- 56 P. Melo Bravo and D. P. Debecker, *Waste Disposal Sustainable Energy*, 2019, **1**, 53–65.
- 57 A. I. Tsiotsias, N. D. Charisiou, I. V. Yentekakis and M. A. Goula, *Catalysts*, 2020, **10**, 812.
- 58 W. J. Tan and P. Gunawan, *Inorganics*, 2023, **11**, 464.
- 59 A. Braga, M. Danielis, S. Colussi and A. Trovarelli, *RSC Mechanochem.*, 2025, **2**, 516–528.
- 60 M. Danielis, S. Colussi, N. J. Divins, L. Soler, A. Trovarelli and J. Llorca, *Johnson Matthey Technol. Rev.*, 2024, **68**, 217–231.
- 61 M. Danielis, L. P. Merkouri, A. Braga, A. Trovarelli, M. S. Duyar and S. Colussi, *J. CO₂ Util.*, 2024, **86**, 102895.
- 62 A. P. Amrute, J. De Bellis, M. Felderhoff and F. Schüth, *Chem.–Eur. J.*, 2021, **27**, 6819–6847.
- 63 J. L. Do and T. Frišćić, *ACS Cent. Sci.*, 2017, **3**, 13–19.
- 64 M. Danielis, J. D. Jiménez, N. Rui, J. Moncada, L. E. Betancourt, A. Trovarelli, J. A. Rodríguez, S. D. Senanayake and S. Colussi, *Appl. Catal., A*, 2023, **660**, 119185.
- 65 J. D. Jiménez, L. E. Betancourt, M. Danielis, H. Zhang, F. Zhang, I. Orozco, W. Xu, J. Llorca, P. Liu, A. Trovarelli, J. A. Rodríguez, S. Colussi and S. D. Senanayake, *ACS Catal.*, 2022, **12**, 12809–12822.
- 66 A. Braga, M. Armengol-Profítos, L. Pascua-Solé, X. Vendrell, L. Soler, I. Serrano, I. J. Villar-García, V. Pérez-Dieste, N. J. Divins and J. Llorca, *ACS Appl. Nano Mater.*, 2023, **6**, 7173–7185.
- 67 Y. Huang, W. Liu, J. Y. Yong, X. J. Zhang, C. Wu and L. Jiang, *Renewable Sustainable Energy Rev.*, 2025, **208**, 115029.
- 68 J. D. Jiménez, L. E. Betancourt, M. Danielis, H. Zhang, F. Zhang, I. Orozco, W. Xu, J. Llorca, P. Liu, A. Trovarelli, J. A. Rodríguez, S. Colussi and S. D. Senanayake, *ACS Catal.*, 2022, **12**, 12809–12822.
- 69 L.-P. Merkouri, E. le Sache, L. Pastor-Perez, M. S. Duyar and T. R. Reina, *Fuel*, 2022, **315**, 123097.
- 70 M. Danielis, S. Colussi, C. de Leitenburg and A. Trovarelli, *Catal. Commun.*, 2020, **135**, 105899.
- 71 M. Danielis, L. E. Betancourt, I. Orozco, N. J. Divins, J. Llorca, J. A. Rodríguez, S. D. Senanayake, S. Colussi and A. Trovarelli, *Appl. Catal., B*, 2021, **282**, 119567.
- 72 S. Colussi, A. Gayen, M. F. Camellone, M. Boaro, J. Llorca, S. Fabris and A. Trovarelli, *Angew. Chem., Int. Ed.*, 2009, **48**, 8481–8484.
- 73 M. Danielis, A. Braga, N. J. Divins, J. Llorca, A. Trovarelli and S. Colussi, *Crystals*, 2023, **13**, 1–16.
- 74 L.-P. Merkouri, J. L. Martín-Espejo, L. F. Bobadilla, J. A. Odriozola, M. S. Duyar and T. R. Reina, *Nanomaterials*, 2023, **13**, 506.
- 75 A. Bermejo-López, B. Pereda-Ayo, J. A. Onrubia-Calvo, J. A. González-Marcos and J. R. González-Velasco, *J. CO₂ Util.*, 2022, **58**, 101922.
- 76 J. Hu, P. Hongmanorom, V. V. Galvita, Z. Li and S. Kawi, *Appl. Catal., B*, 2021, **284**, 119734.
- 77 A. Bermejo-López, B. Pereda-Ayo, J. A. González-Marcos and J. R. González-Velasco, *J. CO₂ Util.*, 2019, **34**, 576–587.
- 78 A. Al-Mamoori, A. A. Rownaghi and F. Rezaei, *ACS Sustain. Chem. Eng.*, 2018, **6**, 13551–13561.
- 79 A. Porta, R. Matarrese, C. G. Visconti, L. Castoldi and L. Lietti, *Ind. Eng. Chem. Res.*, 2021, **60**, 6706–6718.
- 80 A. S. Al-Fatesh, N. Patel, A. H. Fakeeha, M. F. Alotibi, S. B. Alreshaidan and R. Kumar, *Catal. Rev.: Sci. Eng.*, 2023, **66**, 1–99.
- 81 D. Pakhare and J. Spivey, *Chem. Soc. Rev.*, 2014, **43**, 7813–7837.
- 82 T. Sasayama, F. Kosaka, Y. Liu, T. Yamaguchi, S. Y. Chen, T. Mochizuki, A. Urakawa and K. Kuramoto, *J. CO₂ Util.*, 2022, **60**, 102049.
- 83 T. Sasayama, Y. Ono, F. Kosaka, Y. Liu, S. Y. Chen, T. Mochizuki, K. Matsuoka, A. Urakawa and K. Kuramoto, *Sep. Purif. Technol.*, 2025, **354**, 128602.
- 84 N. D. Charisiou, A. Baklavariadis, V. G. Papadakis and M. A. Goula, *Waste Biomass Valorization*, 2016, **7**, 725–736.
- 85 S. Das, J. Ashok, Z. Bian, N. Dewangan, M. H. Wai, Y. Du, A. Borgna, K. Hidajat and S. Kawi, *Appl. Catal., B*, 2018, **230**, 220–236.
- 86 T. Stroud, T. J. Smith, E. Le Saché, J. L. Santos, M. A. Centeno, H. Arellano-García, J. A. Odriozola and T. R. Reina, *Appl. Catal., B*, 2018, **224**, 125–135.
- 87 L.-P. Merkouri, J. L. Martín-Espejo, L. F. Bobadilla, A. Penkova, T. R. Ramirez and J. A. Odriozola, *J. Mater. Chem. A*, 2023, **11**, 13209–13216.
- 88 L.-P. Merkouri, L. Francisco, J. L. Martín-Espejo, A. Penkova, G. Torres-Sempere, M. Short and M. S. Duyar, *Appl. Catal., B: Environ. Energy*, 2025, **361**, 124610.
- 89 L. Hu and A. Urakawa, *J. CO₂ Util.*, 2018, **25**, 323–329.
- 90 M. A. Álvarez, L. F. Bobadilla, V. Garcilaso, M. A. Centeno and J. A. Odriozola, *J. CO₂ Util.*, 2018, **24**, 509–515.
- 91 L. Proaño, E. Tello, M. A. Arellano-Trevino, S. Wang, R. J. Farrauto and M. Cobo, *Appl. Surf. Sci.*, 2019, **479**, 25–30.
- 92 L. Proaño, M. A. Arellano-Treviño, R. J. Farrauto, M. Figueredo, C. Jeong-Potter and M. Cobo, *Appl. Surf. Sci.*, 2020, **533**, 147469.
- 93 H. Sun, J. Wang, J. Zhao, B. Shen, J. Shi, J. Huang and C. Wu, *Appl. Catal., B*, 2019, **244**, 63–75.
- 94 S. Sun, S. He and C. Wu, *Chem. Eng. J.*, 2022, **441**, 135752.
- 95 S. Sun, C. Zhang, S. Guan, S. Xu, P. T. Williams and C. Wu, *Sep. Purif. Technol.*, 2022, **298**, 121604.
- 96 S. Sun, C. Zhang, S. Chen, X. Zhao, Y. Wang, S. Xu and C. Wu, *R. Soc. Open Sci.*, 2023, **10**, 230067.
- 97 H. Sun, Y. Zhang, C. Wang, M. A. Isaacs, A. I. Osman, Y. Wang, D. Rooney, Y. Wang, Z. Yan, C. M. A. Parlett, F. Wang and C. Wu, *Chem. Eng. J.*, 2022, **437**, 135394.
- 98 J. Gandara-Loe, Q. Zhang, J. J. Villora-Picó, A. Sepúlveda-Escribano, L. Pastor-Pérez and T. Ramirez Reina, *Energy Fuels*, 2022, **36**, 6362–6373.
- 99 Y. Han, M. Tian, C. Wang, Y. Kang, L. Kang, Y. Su, C. Huang, T. Zong, J. Lin, B. Hou, X. Pan and X. Wang, *ACS Sustain. Chem. Eng.*, 2021, **9**, 17276–17288.
- 100 M. D. Argyle and C. H. Bartholomew, *Catalysts*, 2015, **5**, 145–269.
- 101 C. H. Bartholomew, in *Catalysis: Volume 10*, Royal Society of Chemistry, 1993, pp. 41–82.

