

Integrated CO₂ capture and utilization with CaO-alone for high purity syngas production

Shuzhuang Sun¹, Zongze Lv², Yuanting Qiao¹, Changlei Qin^{2,*}, Shaojun Xu^{3,4,*}, Chunfei Wu^{1,*}

¹ School of Chemistry and Chemical Engineering, Queen's University Belfast; Belfast, BT7 1NN, UK

² Key Laboratory of Low-grade Energy Utilization Technologies and Systems of Ministry of Education, School of Energy and Power Engineering, Chongqing University; Chongqing 400044, China

³ School of Chemistry, Cardiff University; Cardiff, CF10 3AT, UK

⁴ UK Catalysis Hub, Research Complex at Harwell; Didcot, OX11 0FA, UK



A B S T R A C T

Carbon capture and utilization (CCU) represent a promising strategy to reduce CO₂ emissions and promote a sustainable economy. We report an integrated CCU (ICCU) process by integrating CO₂ capture with reverse water gas shift reaction by applying simple and low-cost CaO as both sorbent and catalyst. By switching the feeding gas from CO₂ source to H₂ isothermally, up to 75% of captured CO₂ was 100% converted into CO at 600–700 °C and the cycle performance of CaO was significantly improved under ICCU condition. In addition, the simulation confirms the significant economic advantage compared to similar traditional processes. The work could dramatically reduce the cost of materials and simplify CCU processes to advance the development and deployment of carbon neutrality technologies.

One-Sentence Summary: A low-cost and widely used material, CaO, was used to not only adsorb CO₂ efficiently but also in situ convert CO₂ into valuable syngas with > 75% CO₂ conversion to realise carbon neutrality, which is a vital target for sustainable future development.

Global climate change is one of the most challenging issues facing the world today, such as ocean acidification (Doney et al., 2009), sea-level increase (Tripathi et al., 2009) and extreme weather (Cai et al., 2015) etc. These changes result from the vast emissions of CO₂ (Blamey et al., 2010). In the last half-century, the concentration of CO₂ has exhibited a dramatic increase from ca. 310 to over 410 ppm owing to the large-scale utilization of fossil fuels and various chemical refinery processes (Lackner, 2003, Yu et al., 2008, Hu et al., 2016). Carbon capture and utilization (CCU) has a great potential to develop a circular economy and mitigate global warming. CO₂ could be an efficient energy storage chemical if used to produce fuels and chemicals with a high energy density (Buelens et al., 2016). Although CO₂ is a thermodynamically and chemically stable molecule under standard conditions, CCU represents an attractive carbon building block in organic synthesis to mitigate climate change.

Typically, CCU has a few steps, including CO₂ capture, storage, transportation, and utilization. The current state-of-the-art CCU process, including CO₂ capture and CO₂ utilization, is researched separately. Thus, a large amount of energy is required for CO₂ storage and transportation. Recently, CO₂ capture and utilization have been integrated (Sun et al., 2019, Sun et al., 2021, Sun et al., 2020). In the integrated CO₂ capture and utilization (ICCU) process, dual functional materials (DFMs), a combination of sorbent and catalyst, can capture CO₂ from flue gas. After CO₂ capture, a reducing agent (e.g. H₂) can regenerate the DFMs and simultaneously convert the captured CO₂ into valuable chemicals (e.g.

CO). For both conventional and integrated CCU, the utilization of CO₂ requires a catalyst and sorbent.

Furthermore, a transition-metal-based catalyst (e.g. Ni-, Cu- and Ru-based) is known to be essential (De et al., 2020, Chen et al., 2020, Zhang et al., 2020). However, the deactivation of transition-metal-based catalysts is common and is a significant challenge for CO₂ utilization. Besides, these catalysts have high costs and cause environmental pollution during the preparation and disposal of catalysts. Thus, finding efficient non-transition-metal-based catalysts for CO₂ utilisation will be promising and essential for CCU development.

Here we report a novel ICCU process using environmental-friendly, and cost-effective CaCO₃ derived CaO as both effective adsorbent and highly efficient catalyst to produce high purity syngas. The proposed process vastly reduces the material cost for ICCU and effectively mitigates the challenges in the deactivation of transition-metal-based DFMs in conventional CCU processes. As an adsorbent and catalyst, CaO experimentally achieved impressive carbon processing throughput, CO₂ conversion (> 75%) and CO yield (Fig. 1). In this work, the reaction temperature has shown a significant effect on the ICCU performance. A higher temperature is more active for CO generation, yielding 0.34, 1.53 and 4.15 mmol/g_{CaO} at 600, 650 and 700 °C in 28 mins, respectively. In contrast, CO₂ conversion is slightly decreased with the increase of reaction temperature, from 88.09% at 600 °C to 75.48% at 700 °C (Fig. 1) due to the enhanced CO₂ desorption kinetics. Furthermore, CH₄ is not detected in the overall conversion process and CO₂ was completely converted to CO.

* Corresponding author.

E-mail addresses: c.qin@cqu.edu.cn (C. Qin), XuS25@cardiff.ac.uk (S. Xu), c.wu@qub.ac.uk (C. Wu).

<https://doi.org/10.1016/j.ccst.2021.100001>

Received 28 June 2021; Received in revised form 23 July 2021; Accepted 23 August 2021

2772-6568/© 2021 The Author(s). Published by Elsevier Ltd on behalf of Institution of Chemical Engineers (IChemE). This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>)

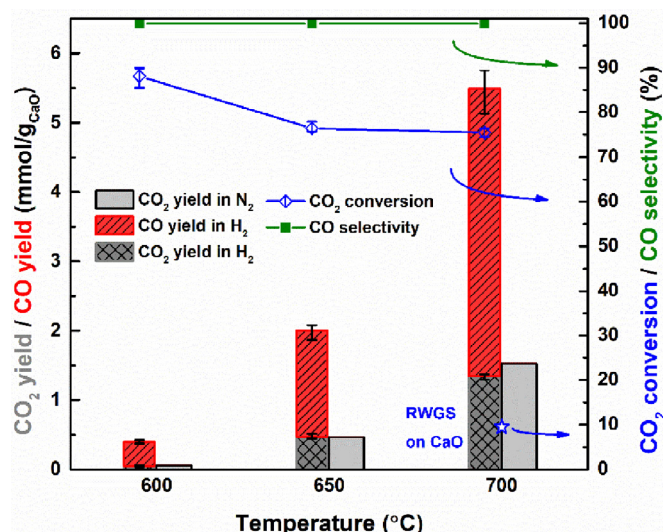


Fig. 1. The yield, conversion and selectivity of CO₂ and CO in ICCU using CaO alone. (ICCU over CaO: 500ml/min 15%CO₂/N₂ carbonation for 30 min, N₂ purge for 2 min, 500ml/min H₂ regeneration for 28 min, cat.= 5.0g CaO; RWGS over CaO: H₂/CO₂=4:1, cat.= 5.0g CaO)

By investigating the reaction mechanism using in-situ diffused reflectance infrared Fourier transform spectroscopy coupled with mass spectrum (DRIFTS-MS), we confirm the formation of calcium carbon-

ate (CaCO₃) during the CO₂ adsorption (character peaks assigned in Fig. S4a). And we found the direct reaction between H₂ and carbonates by the dissociation of carbonates into surface hydroxyl and CO (fig. S4b). It is noted that the conversion of CO₂ in the ICCU process using CaO-alone is still higher than most of the reported CO₂ conversion from conventional reverse-water-gas shift reaction (RWGS) where transition-metal-based catalysts were used (fig. S8) (Daza and Kuhn, 2016). We further replaced H₂ with N₂ to confirm the exceptional performance of CaO in ICCU, and there is no distinct CO production in the presence of N₂. It is interesting to observe that the yield of CO₂ is similar in both N₂ and H₂ atmosphere during the utilization stage of ICCU. For example, the yield of CO₂ is 1.34 and 1.53 mmol/g_{CaO}, and the yield of CO is 4.15 and 0.01 mmol/g_{CaO} at 700 °C in H₂ and N₂, respectively. Therefore, it is proposed that CaO acts as CO₂ adsorbent and catalyses CO₂ for producing CO by directly reducing carbonates with the assistance of H₂, which is also confirmed by in situ DRIFTS-MS (fig. S4b and S4c). The ICCU mechanism of CO₂ adsorption over CaO and the H₂ regeneration of CaCO₃ were proposed in fig S5 and discussed in Supplementary Text. Typically, the extensive hydroxyl groups in the initial hydrogenation stage indicate the effective H₂ dissociation on the surface of CaCO₃, and the CO can be dissociated from the hydrogenated carbonate and released out quickly. The formates species or the hydrogenated carbonate (as shown in Fig. S5) might be the critical intermediates. Notably, the CaO used in this work is more cost-effective than the widely used transition metal-based catalysts, while achieving higher CO₂ conversion and excellent CO selectivity (fig. S8). These results demonstrate this simple process's technical and economic advantages from the perspectives of CO₂ conversion, CO selectivity, and low-cost and robust materials.

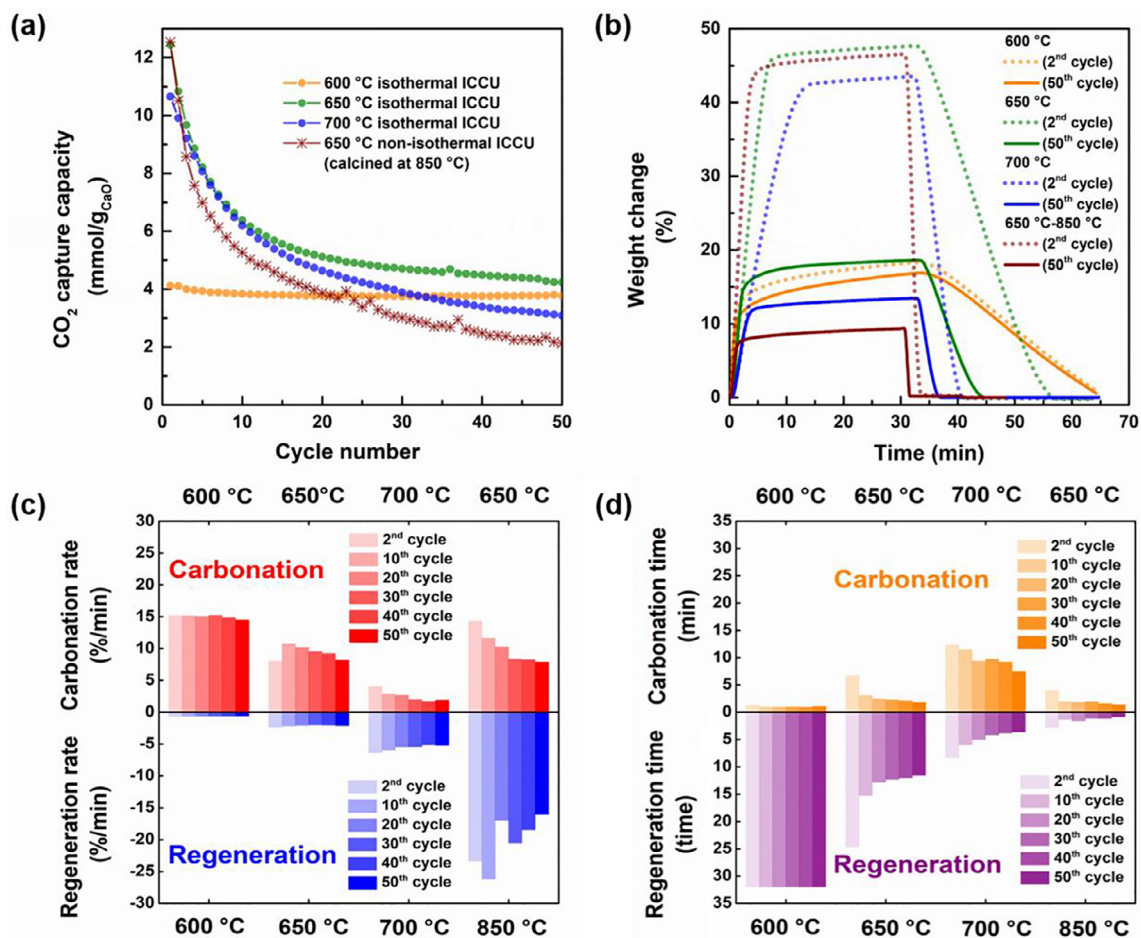


Fig. 2. Cyclic carbonation and H₂-regeneration performance of CaO under isothermal (600 °C, 650 °C and 700 °C) and non-isothermal conditions (carbonate at 650 °C and regenerate at 850 °C). (a) Cyclic capacity of CO₂ capture; (b) Comparison of dynamic profiles of 2nd and 50th cycles; (c) Comparison of carbonation and regeneration rate in cycles; (d) Comparison of carbonation and regeneration time in cycles. (carbonation rates and times were calculated from the rapid adsorption stage)

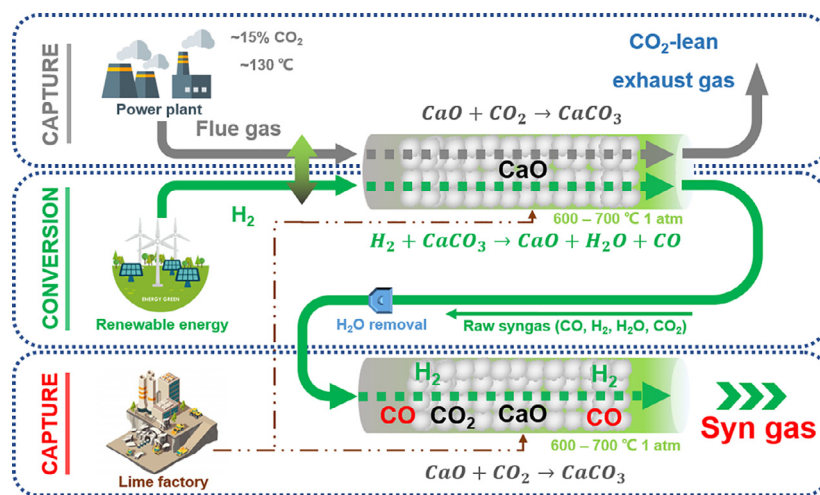


Fig. 3. Schematic diagram of improved ICCU process

The excellent performance of CaO-alone in ICCU has been extended to its stability. Using TGA analysis at 600 °C under CO₂ and H₂ switching, we obtain a very stable ICCU performance after 154 cycles of carbonation and regeneration in relation to weight changes, reducing from 4.1 mmol/g_{CaO} in the 1st cycle to 3.6 mmol/g_{CaO} in the 150th cycle (Fig. 2a and fig. S13). The lower initial adsorption capacity at 600 °C is mainly caused by the slow kinetics of CaCO₃ regeneration. That is, CaO can not fully return to the initial state before the 2nd carbonation cycle (fig. S13). However, such incomplete desorption has shown extremely excellent cyclic performance. In contrast, higher initial adsorption capacities are obtained at 650 °C and 700 °C (12.44 and 10.66 mmol/g_{CaO} in the 1st cycle, respectively) due to the enhanced kinetics (fig. S14 and S15). However, the capacity of CO₂ capture is significantly reduced in the initial 30 cycles, decreasing to 5 and 4 mmol/g_{CaO} at 650 °C and 700 °C, respectively. In terms of long-term stability, the cycle performance at 600 °C is superior to 650 °C and 700 °C, corresponding to 3.72, 3.61 and 2.12 mmol/g_{CaO} after 120 cycles, respectively. The severity of sintering under various temperatures can be clearly observed from SEM (fig. S17). The above results demonstrate both acceptable adsorption performance and the long-term stability of CaO under isothermal conditions.

We further investigated the influence of regeneration temperature on the performance of CaO. After 50 cycles of ICCU, the regeneration of CaO at 850 °C in H₂ results in a significant reduction of CO₂ capture capacity from 12.45 to 2.12 mmol/g_{CaO} (Fig. 2a). This is due to the sintering of CaO particles at high regeneration temperature (Valverde et al., 2014) (fig. S17e). In addition, we investigated the kinetic performance for carbonation and H₂ regeneration (Fig. 2b, 2c and 2d). The carbonation rate of rapid adsorption is decreased with the increase of carbonation temperature, while the carbonation time is prolonged. The carbonation kinetics are directly related to the efficiency of industrial applications, represented by the flue gas throughput of per unit of CaO at per unit time. Compared to the carbonation rate, faster regeneration is more correlated to the deactivation of CaO derived from the fast volume shrinkage from CaCO₃ (36.9 cm³/mol) to CaO (16.9 cm³/mol) (Fig. 2c) (Dean et al., 2011).

In addition, regenerating CaO in CO₂ should be responsible for the deactivation of CaO (Dean et al., 2011, Perejon et al., 2016). By changing the regeneration atmosphere from H₂ to CO₂ at 850 °C, we observe rapid deactivation, especially in the initial 30 cycles (fig. S16a). Therefore, the deactivation of CaO can be effectively prohibited in H₂ regeneration. More importantly, the regeneration of CaO under H₂ could well retain the characteristics of rapid adsorption of CaO in cycles of carbonation and regeneration (fig. S16b), which is beneficial for practical applications by shortening the carbonation stage.

Based on the above results, we propose an improved ICCU process including CO₂ capture, conversion and re-capture to deliver pure syn-

gas from flue gas (as illustrated in Fig. 3). The improved ICCU process has three steps, including 1) using CaO-alone to capture CO₂ from flue gas to reduce CO₂ emission; 2) using the mixture of CaO/CaCO₃ as the catalyst to regenerate CaCO₃ and to convert the captured CO₂ into CO by switching gas to H₂; 3) using another same CaO bed as a sorbent to remove un-reacted CO₂ to produce pure syngas, and the saturated CaO can be similarly regenerated by introducing H₂. Since no other metal catalysts are added, the deactivated CaO can be used for cement manufacturing to avoid secondary pollution.

Using Aspen Plus® to model and simulate the proposed ICCU process, the techno-economic advantages of using CaO-alone are confirmed to deliver efficient carbon capture and utilization. The results show that the cost of producing CO is 292\$/ton for the improved ICCU process, which is much lower than the reference scenario (447\$/ton), including conventional calcium looping, combined with CO₂ transportation, storage, RWGS and syngas purification. It is noted that only materials and utility costs are considered here. In addition, the cost of CO₂ avoidance of ICCU is reduced from 272 to 184\$/ton compared to the reference scenario. The energy efficiency (power production over thermal energy input) is also improved from 20% to 25% without the consideration of heat recovery when the improved ICCU process is applied compared to the conventional CCU. The critical saving of the improved ICCU process is related to the low cost of materials, the reduction of CO₂ storage and transportation and the intensification of carbon capture and utilization.

To summarize, we experimentally demonstrated the feasibility of a novel ICCU process for producing syngas from CO₂ sources from integrated CO₂ capture and utilization using CaO-alone. The proposed novel concept significantly improves the cycle stability of CaO in carbon capture and shortens the whole process to capture and utilize CO₂ directly from flue gas. We also demonstrated the advantages of producing pure syngas with CaO-alone using the ICCU process through Aspen Plus® modelling. The produced syngas can be used for liquid fuel production from commercial processes such as Fischer–Tropsch synthesis.

Declaration of Competing Interest

Authors declare that they have no competing interests.

CRediT authorship contribution statement

Shuzhuang Sun: Conceptualization, Data curation, Formal analysis, Investigation, Methodology. **Zongze Lv:** Data curation, Investigation, Validation, Visualization, Writing – original draft, Writing – review & editing. **Yuanting Qiao:** Formal analysis, Resources. **Changlei Qin:** Methodology, Resources, Supervision, Validation, Writing – review & editing. **Shaojun Xu:** Data curation, Investigation, Resources, Supervi-

sion, Visualization, Writing – review & editing. **Chunfei Wu:** Conceptualization, Funding acquisition, Methodology, Project administration, Resources, Supervision, Writing – review & editing.

Acknowledgements

The authors gratefully acknowledge financial support from the China Scholarship Council (reference number:201906450023). This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 823745. This research has been performed with the use of facilities at the Research Complex at Harwell including 'Scanning electron microscope' equipment. The authors would like to thank the Research Complex for access and support to these facilities and equipment.

Funding

China Scholarship Council grant 201906450023
Marie Skłodowska-Curie grant No 823745

Data and materials availability

All data are available in the main text or the supplementary materials.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.ccs.2021.100001](https://doi.org/10.1016/j.ccs.2021.100001).

References

- Blamey, J., Anthony, E.J., Wang, J., Fennell, P.S., 2010. The calcium looping cycle for large-scale CO₂ capture. *Progress in Energy and Combustion Science* 36, 260–279. doi:[10.1016/j.pecs.2009.10.001](https://doi.org/10.1016/j.pecs.2009.10.001), <https://doi.org/>.
- Buelens, L.C., Galvita, V.V., Poelman, H., Detavernier, C., Marin, G.B., 2016. Super-dry reforming of methane intensifies CO₂ utilization via Le Chatelier's principle. *Science* doi:[10.1126/science.aah7161](https://doi.org/10.1126/science.aah7161), <https://doi.org/>.
- Cai, W., Santoso, A., Wang, G., Yeh, S.-W., An, S.-I., Cobb, K.M., Collins, M., Guilyardi, E., Jin, F.-F., Kug, J.-S., 2015. ENSO and greenhouse warming. *Nature Climate Change* 5, 849–859. doi:[10.1038/nclimate2743](https://doi.org/10.1038/nclimate2743), <https://doi.org/>.
- Chen, B.F., Dong, M.H., Liu, S.L., Xie, Z.B., Yang, J.J., Li, S.P., Wang, Y.Y., Du, J., Liu, H.Z., Han, B.X., 2020. CO₂ Hydrogenation to Formate Catalyzed by Ru Coordinated with a N,P-Containing Polymer. *ACS Catalysis* 10, 8557–8566. doi:[10.1021/acscatal.0c01678](https://doi.org/10.1021/acscatal.0c01678), <https://doi.org/>.
- Daza, Y.A., Kuhn, J.N., 2016. CO₂ conversion by reverse water gas shift catalysis: comparison of catalysts, mechanisms and their consequences for CO₂ conversion to liquid fuels. *Rsc Advances* 6, 49675–49691. doi:[10.1039/c6ra05414e](https://doi.org/10.1039/c6ra05414e), <https://doi.org/>.
- De, S., Dokania, A., Ramirez, A., Gascon, J., 2020. Advances in the Design of Heterogeneous Catalysts and Thermocatalytic Processes for CO₂ Utilization. *ACS Catalysis* 10, 14147–14185. doi:[10.1021/acscatal.0c04273](https://doi.org/10.1021/acscatal.0c04273), <https://doi.org/>.
- Dean, C.C., Blamey, J., Florin, N.H., Al-Jeboori, M.J., Fennell, P.S., 2011. The calcium looping cycle for CO₂ capture from power generation, cement manufacture and hydrogen production. *Chemical Engineering Research & Design* 89, 836–855. doi:[10.1016/j.cherd.2010.10.013](https://doi.org/10.1016/j.cherd.2010.10.013), <https://doi.org/>.
- Doney, S.C., Fabry, V.J., Feely, R.A., Kleypas, J.A., 2009. Ocean acidification: the other CO₂ problem. *Annual Review of Marine Science* 1, 169–192. doi:[10.1146/annurev.marine.010908.163834](https://doi.org/10.1146/annurev.marine.010908.163834), <https://doi.org/>.
- Hu, Y., Liu, W., Chen, H., Zhou, Z., Wang, W., Sun, J., Yang, X., Li, X., Xu, M., 2016. Screening of inert solid supports for CaO-based sorbents for high temperature CO₂ capture. *Fuel* 181, 199–206. doi:[10.1016/j.fuel.2016.04.138](https://doi.org/10.1016/j.fuel.2016.04.138), <https://doi.org/>.
- Lackner, K.S., 2003. A guide to CO₂ sequestration. *Science* 300, 1677–1678. doi:[10.1126/science.1079033](https://doi.org/10.1126/science.1079033), <https://doi.org/>.
- Perejon, A., Romeo, L.M., Lara, Y., Lisbona, P., Martinez, A., Valverde, J.M., 2016. The Calcium-Looping technology for CO₂ capture: On the important roles of energy integration and sorbent behavior. *Applied Energy* 162, 787–807. doi:[10.1016/j.apenergy.2015.10.121](https://doi.org/10.1016/j.apenergy.2015.10.121), <https://doi.org/>.
- Sun, H., Wang, J., Zhao, J., Shen, B., Shi, J., Huang, J., Wu, C., 2019. Dual functional catalytic materials of Ni over Ce-modified CaO sorbents for integrated CO₂ capture and conversion. *Applied Catalysis B: Environmental* 244, 63–75. doi:[10.1016/j.apcatb.2018.11.040](https://doi.org/10.1016/j.apcatb.2018.11.040), <https://doi.org/>.
- Sun, H., Wang, Y., Xu, S., Osman, A.I., Stenning, G., Han, J., Sun, S., Rooney, D., Williams, P.T., Wang, F., Wu, C., 2021. Understanding the interaction between active sites and sorbents during the integrated carbon capture and utilization process. *Fuel* 286, 119308. doi:[10.1016/j.fuel.2020.119308](https://doi.org/10.1016/j.fuel.2020.119308), <https://doi.org/>.
- Sun, H., Zhang, Y., Guan, S., Huang, J., Wu, C., 2020. Direct and highly selective conversion of captured CO₂ into methane through integrated carbon capture and utilization over dual functional materials. *Journal of CO₂ Utilization* 38, 262–272. doi:[10.1016/j.jcou.2020.02.001](https://doi.org/10.1016/j.jcou.2020.02.001), <https://doi.org/>.
- Tripati, A.K., Roberts, C.D., Eagle, R.A., 2009. Coupling of CO₂ and ice sheet stability over major climate transitions of the last 20 million years. *Science* 326, 1394–1397. doi:[10.1126/science.1178296](https://doi.org/10.1126/science.1178296), <https://doi.org/>.
- Valverde, J.M., Sanchez-Jimenez, P.E., Perez-Maqueda, L.A., 2014. Calcium-looping for post-combustion CO₂ capture. On the adverse effect of sorbent regeneration under CO₂. *Applied Energy* 126, 161–171. doi:[10.1016/j.apenergy.2014.03.081](https://doi.org/10.1016/j.apenergy.2014.03.081), <https://doi.org/>.
- Yu, K., Curcic, I., Gabriel, J., Tsang, S., 2008. Recent advances in CO₂ capture and utilization. *ChemSusChem* 1, 893–899. doi:[10.1002/cssc.200800169](https://doi.org/10.1002/cssc.200800169), <https://doi.org/>.
- Zhang, J.C., Ge, B.H., Liu, T.F., Yang, Y.Z., Li, B., Li, W.Z., 2020. Robust Ruthenium-Saving Catalyst for High-Temperature Carbon Dioxide Reforming of Methane. *ACS Catalysis* 10, 783–791. doi:[10.1021/acscatal.9b03709](https://doi.org/10.1021/acscatal.9b03709), <https://doi.org/>.