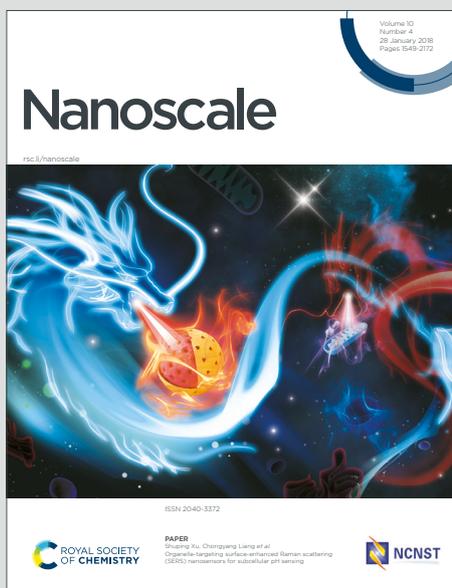


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ARTICLE

Bimetallic RuNi-Decorated Mg-CUK-1 for Oxygen-Tolerant Carbon Dioxide Capture and Conversion to Methane

Timothy Zurrer^a, Emma Lovell^a, Zhaojun Han^{a,b}, Kang Liang^{a,c}, Jason Scott^{*a} and Rose Amal^{*a}

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The development of hybrid sorbent/catalysts for carbon capture and conversion to chemical fuels involves several material and engineering design considerations. Herein, a metal-organic framework (MOF), known as Mg-CUK-1, is loaded with Ru and Ni nanoparticles and assessed as a hybrid material for the sequential capture and conversion of carbon dioxide (CO₂) to methane (CH₄). Low nanocatalyst loadings led to enhanced overall performance by preserving more CO₂ uptake within the Mg-CUK-1 sorbent. Low temperature CO₂ desorption from Mg-CUK-1 facilitated complete CO₂ release and subsequent conversion to CH₄. The influence of oxygen exposure on catalyst performance was assessed, with Ru-loaded Mg-CUK-1 exhibiting oxygen tolerance through sustained CH₄ generation of 1.40 mmol g⁻¹ over ten cycles. In contrast, Ni-loaded Mg-CUK-1 was unable to retain initial catalytic performance, reflected in an 11.4% decrease in CH₄ generation over ten cycles. When combined, 0.3Ru2.7Ni Mg-CUK-1 yielded comparable overall performance to 3Ru Mg-CUK-1, indicating that Ru aids the re-reduction of NiO to Ni after O₂ exposure. By combining multiple catalyst species within one hybrid sorbent/catalyst material, greater catalyst stability is achieved, resulting in sustained overall performance. The introduced strategy provides an approach for fostering resilient hydrogenation catalysts upon exposure to reactive species often found in real-world point source CO₂ emissions.

1. Introduction

The Intergovernmental Panel on Climate Change's (IPCC) Sixth Assessment report highlights the need for a diverse range of carbon capture technologies to restrict rising atmospheric CO₂ levels and limit outcomes associated with increasing global temperatures.¹ Carbon capture and conversion to chemical fuels represents a promising mitigation strategy within a broader suite of carbon capture and utilisation (CCU) approaches. By reacting captured CO₂ with green H₂, the resulting fuel can act as an energy carrier easily integrated into existing supply chains for CH₄ and CH₃OH.^{2, 3} The primary challenge associated with CO₂ hydrogenation reactions is the significant energy requirement that needs to be overcome to deliver adequate fuel production for industrial implementation. Metal-based catalysts have been used to overcome the otherwise prohibitively large energetic barrier and are often loaded onto metal oxides to preserve nanoparticle dispersion.⁴

Integrating adsorption-based carbon capture into CO₂ hydrogenation catalytic systems represents a recent trend in CCU research.⁵⁻⁷ The benefit of system integration allows for a

streamlined unit with a minimized physical footprint, particularly suited for modular, distributed systems in urban areas. When co-located with point source CO₂ emissions, modular CCU units can eliminate the need for CO₂ transport, helping to reduce ancillary greenhouse gas emissions associated with operation.

Despite several potential advantages, there remain distinct challenges when developing integrated carbon capture and hydrogenation systems. The design of hybrid CO₂ sorbent/catalyst materials is one such challenge. When cycling between carbon capture and conversion modes, reactive species have the potential to poison the included catalyst, limiting its long-term recyclability. Reduced chemical fuel yield over repeated cycles can dramatically impact overall performance with more frequent catalyst replacement leading to increased operating costs. Therefore, developing catalysts that can withstand exposure to industrially available CO₂ streams comprised of O₂, SO_x, NO_x and other reactive species needs to be addressed.

To date, hybrid sorbent/catalyst materials have focused on using metal oxides, metal carbonates and metal bicarbonates as CO₂ capture agents.⁸⁻²³ Once the sorbent reaches saturation through the formation of carbonate or bicarbonate species; the reactor system is heated to an appropriate reaction temperature (300-400 °C), where H₂ is introduced to generate CH₄. However, due to the strong carbonate/bicarbonate chemical bonds created during carbon uptake, high temperatures are necessary to completely desorb the bound

^a School of Chemical Engineering, The University of New South Wales (UNSW) Sydney, NSW 2052, Australia

^b CSIRO Manufacturing, 36 Bradfield Road, Lindfield, NSW 2070, Australia

^c Graduate School of Biomedical Engineering, The University of New South Wales (UNSW) Sydney, NSW 2052, Australia

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CO₂ so it is available for hydrogenation.^{24, 25} Increased reaction temperatures undesirably raise the system's energy footprint while also introducing the likelihood of the reverse water-gas shift side reaction taking place.^{4, 26} Even at high temperatures, incomplete CO₂ desorption has been observed in metal oxide-based hybrid sorbent/catalyst systems.^{13-15, 18-20, 27-29}

To overcome these challenges, using physisorption-based carbon capture agents in hybrid sorbent/catalysts is advantageous due to complete CO₂ desorption below typical CO₂ hydrogenation reaction temperatures. Metal-organic frameworks represent a class of materials demonstrating large physisorption-led CO₂ uptakes.³⁰⁻³² MOFs also offer significant design flexibility through careful selection of the included metal ion and organic linker components.³³⁻³⁶ Selecting an appropriate MOF capable of substantial CO₂ adsorption capacity, robust thermal stability and structural resilience to reactive gas-phase species is central to furthering the design of hybrid sorbent/catalyst materials. MOFs have also emerged as nanocatalyst supports for CO₂ hydrogenation reactions, presenting distinct mechanistic pathways from conventional metal/metal oxide systems.^{37, 38} Understanding metal-support interactions involving MOFs remains an emerging area of investigation.

Mg-CUK-1 [Mg₃(μ₃-OH)₂(2,4-pdc)₂; 2,4-pdc = 2,4-pyridine dicarboxylate] is a thermally stable MOF that has previously been investigated as a CO₂ physisorbent.³⁹ Enhanced CO₂ uptake by Mg-CUK-1 has been observed in the presence of moisture, with improvement from 4.6 wt% to 8.6 wt% at 20% relative humidity.⁴⁰ H₂O and CO₂ commonly compete for the same adsorption sites in MOFs, hindering their implementation in real-world adsorption scenarios. Given that H₂O is generated during CO₂ hydrogenation reactions, sorbent stability under hydrothermal conditions is an important design consideration. Hydroxyl groups that line the Mg-CUK-1 interior have been deemed responsible for improved CO₂ uptake and offering protection of the linker-node coordination bonds from framework decomposition.⁴¹ The chemical stability of Mg-CUK-1 has also been demonstrated through sustained adsorption/desorption cycling of H₂S and H₂O vapour, with no impact on framework crystallinity or uptake. The combination of hydrothermal stability and suitable CO₂ physisorption renders Mg-CUK-1 an ideal sorbent for combined carbon capture and conversion of CO₂ to chemical fuels.

Several metals, including Ni, Co, Ru, Rh, Pd and Pt, have been investigated as CO₂ hydrogenation catalysts.⁴²⁻⁴⁵ Ni is known to be CH₄ selective and offers competitive activity with platinum group metals (PGM) candidates.^{17, 27, 46} Transition metals such as Ni also benefit from being more abundant and, therefore more cost-effective than PGMs such as Ru. However, transition metals require higher temperatures to undergo reduction once oxidised.⁴⁷ When considering applications where oxygen exposure is unavoidable, such as CO₂ capture from point source emissions, design strategies that improve the oxygen tolerance of Ni are important for maintaining overall system performance.

In this work, Ni and Ru species are loaded into Mg-CUK-1 and the resulting hybrid sorbent/nanocatalyst is appraised for

the capture and conversion of CO₂ into CH₄. The impact of catalyst loading and composition on CO₂ uptake and CH₄ generation is examined separately before being combined into a single reactor unit. The effect of CO₂ stream composition on overall system performance is ascertained, culminating in the evaluation of a dual metal RuNi-loaded Mg-CUK-1 to aid with oxygen tolerance upon exposure to air during carbon capture. By offering insights into the design challenges associated with hybrid sorbent/catalyst materials, we highlight the potential for nanoparticle/MOF composites to maximize overall carbon capture and conversion system performance through judicious material design.

2. Experimental

2.1 Preparation of Mg-CUK-1

The synthesis of Mg-CUK-1 was conducted using a method reported previously.³⁹ A solution of 2,4-pyridine dicarboxylic acid monohydrate (1 mmol, 185 mg) and potassium hydroxide (3 mL, 224 mg) was added to an aqueous solution (3 mL) of magnesium nitrate hexahydrate (1.5 mmol). Once mixed, the reaction solution was transferred into a Teflon-lined autoclave and heated to 200 °C for 15 h. The vessel was allowed to cool slowly over a six-hour timeframe. The resulting crystalline solids were separated through sonication, whereby the cloudy supernatant was drawn off and replenished with deionised H₂O. The solid product was washed three times before being dried in an oven at 100 °C.

2.2 Preparation of Ni- and Ru-loaded Mg-CUK-1

Mg-CUK-1 was loaded with Ni and Ru using a double solvent impregnation approach to promote nanoparticle growth within the hydrophilic MOF interior. Before loading, Mg-CUK-1 was dried under vacuum at 150 °C for 12 h to remove any pre-adsorbed species. A 100 mg of anhydrous Mg-CUK-1 was then suspended in 5 mL of hexane. Next, 22 μL of RuCl₃ or NiCl₂ was added to the hexane/Mg-CUK-1 mixture and allowed to stir overnight to ensure precursor impregnation. A precursor solution of 0.15 mg/mL was used to produce three wt% Ru and Ni-loaded samples, while 0.30 mg/mL was used for the higher loading of 6 wt% Ni and 7 wt% Ru. Corresponding samples are denoted as 3Ru, 3Ni, 6Ni and 7Ru, respectively. A mixed-metal RuNi-loaded Mg-CUK-1 sample was also synthesised with precursor solution concentrations of 0.015 mg/mL and 0.285 mg/mL of Ru and Ni precursor, respectively. Again, 22 μL of precursor solution is added to 100 mg of anhydrous Mg-CUK-1 with the resulting material denoted as 0.3Ru2.7Ni. Once complete, the hexane supernatant was carefully removed, and the samples were initially dried at 80 °C before being transferred to the reactor and pre-treated at 350 °C for 12 h under a reducing atmosphere (30 mL min⁻¹ H₂).

2.3 X-ray diffraction

X-ray diffraction measurements were performed using a PANalytical Xpert Multipurpose X-ray Diffraction System (MPD) operating at 45 kV and 40mA using a Cu Kα radiation source (λ=1.5406 Å). Diffractograms were collected over the 5-90° 2θ

range. Diffraction patterns were analyzed and processed using Highscore Plus software.

2.4 CO₂ adsorption isotherms

CO₂ adsorption isotherms were collected using a Micromeritics TriStar II PLUS instrument at 0 °C. Samples were thermally treated at 150 °C under vacuum (<0.015 kPa) using a Micromeritics Smart VacPrep unit to remove any residual solvent before measurement.

2.5 Transmission electron microscopy

Transmission electron microscopy (TEM) imaging was performed using a JEOL 1400 instrument at 100 kV and 55 μA. High-resolution TEM was completed using a FEI Tecnai G2 20 instrument operating at 200 kV. Before imaging, samples were dispersed in methanol and drop cast onto carbon grids.

2.6 Steady-state CO₂ hydrogenation performance tests

Catalytic performance tests were conducted using 50 mg of sample loaded into a 30 mm long, 6 mm internal diameter quartz tube reactor. Each catalyst was pre-treated at 350 °C under a reducing atmosphere (30 mL min⁻¹ H₂) before performance testing.

Steady-state performance tests were conducted using a feed gas mixture of 50 mL min⁻¹ N₂, 6 mL min⁻¹ CO₂ and 24 mL min⁻¹ H₂. The total flow rate of 80 mL min⁻¹ corresponds to a gas hourly space velocity of 48 L h⁻¹ g_{cat}⁻¹. A temperature controller was used to heat the reactor from 250 °C to 400 °C at a rate of 5 °C min⁻¹ while holding for 30 min at each 50 °C interval.

The gases leaving the reactor were sampled and analysed by two gas chromatographs; a Shimadzu 8A equipped with a thermal conductivity detector (TCD) and Zeolite 13X column for N₂ and H₂ detection and a Shimadzu 2010 fitted with a methanizer and flame ionization detector array and HP/PlotQ column for CH₄, CO₂ and CO detection. The resulting peak areas were translated to flow rates using calibration data. The data was subsequently used to calculate CO₂ conversion and CH₄ selectivity.

2.7 Batch CO₂ capture and conversion performance tests

CO₂ capture and conversion performance tests were conducted in the same reactor set up as the steady state experiments. Initially, 20 mL min⁻¹ CO₂ was passed over the hybrid sorbent/catalyst for 60 min to achieve CO₂ saturation. The system was then flushed with H₂ (30 mL min⁻¹) for 20 min to ensure the only remaining CO₂ in the system was held on the sorbent surface. The system was then switched to recirculation mode whereby the contents of the reactor were cycled repeatedly over the catalyst bed at 50 mL min⁻¹. The reactor was then heated to 300 °C at 20 °C min⁻¹ and held for 10 minutes to allow for methanation to occur. Reactor sampling proceeded for 50 minutes, whereby gas samples were redirected to the gas chromatographs for CO₂ and CH₄ quantification.

A reduced CO₂ flow composition was also incorporated into the batch performance tests, comprising 15% CO₂ (7.5 mL min⁻¹) and the balance air (42.5 mL min⁻¹) to simulate a dry flue gas stream. Once the CO₂ adsorption and conversion stages were

complete, the reactor system was cooled to 25 °C and the adsorption-reaction cycle was repeated.

2.8 X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) was conducted using a Thermo-Fischer ESCALAB250i high-resolution X-ray photoelectron spectrometer equipped with a monochromatic Al Kα soft X-ray source (1486.6 eV). Survey spectra were collected up to 1350 eV binding energy with binding energy values referenced to the C 1s peak at 284.8 eV. Data analysis was conducted using CasaXPS.

3. Results and Discussion

3.1 Hybrid Sorbent/Catalyst Preparation

The sorbent, Mg-CUK-1, was loaded with Ru and Ni using a double-solvent impregnation strategy to promote the formation of nanoparticles within the MOF particle interior. Low catalyst loadings were selected to preserve as much of the accessible surface area of the sorbent as possible. Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) results reported catalyst loadings of 3.1 wt% and 6.22 wt% for 3Ni and 6Ni, respectively, and 3.41 wt% and 7.40 wt% for 3Ru and 7Ru, respectively (Table S1).

Powder X-ray diffraction patterns of Mg-CUK-1 (**Figure 1**) reveal successful MOF self-assembly with peaks closely matching the simulated pattern for Mg-CUK-1 (Figure S1). Once loaded, no peaks associated with Ru or Ni species are observed within the diffraction data, likely due to low catalyst loadings. Importantly, the diffraction peaks associated with Mg-CUK-1 are retained after pre-treatment at 350 °C, indicating that the framework is stable at temperatures necessary for CO₂ hydrogenation.

3.2 Carbon Capture Sorbent Performance

The influence of catalyst loading on CO₂ adsorption capacity is important when formulating hybrid sorbent/catalyst materials. The pristine Mg-CUK-1 possesses the highest CO₂ uptake of 5.28 mmol g⁻¹ at 104.9 kPa and 0 °C (**Figure 2**). For 3Ni and 3Ru, CO₂ adsorption decreases moderately to 4.41 and 4.11 mmol g⁻¹, respectively. The reduction in CO₂ capacity can be attributed to the mass contribution of the metal catalysts and partial pore blockage arising from nanoparticle inclusion. The effect is more pronounced for larger catalyst loadings, with 6Ni and 7Ru possessing a CO₂ uptake of 4.07 mmol g⁻¹ and 3.76 mmol g⁻¹. The slightly lower uptake for materials containing Ru is attributed to the marginally higher loadings reflected in the ICP-OES results (Table S1).

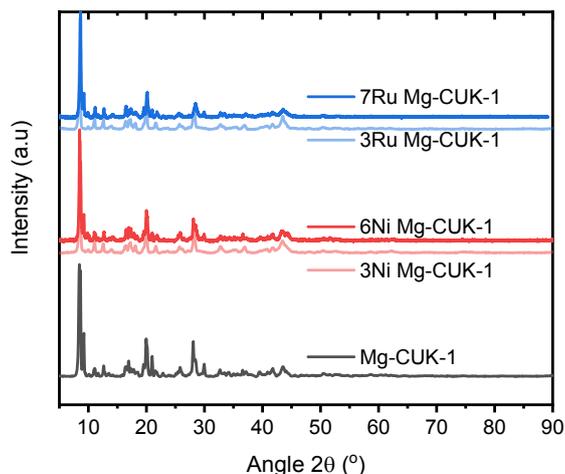


Figure 1. X-ray diffraction patterns of Mg-CUK-1, Ni-loaded Mg-CUK-1 and Ru-loaded Mg-CUK-1.

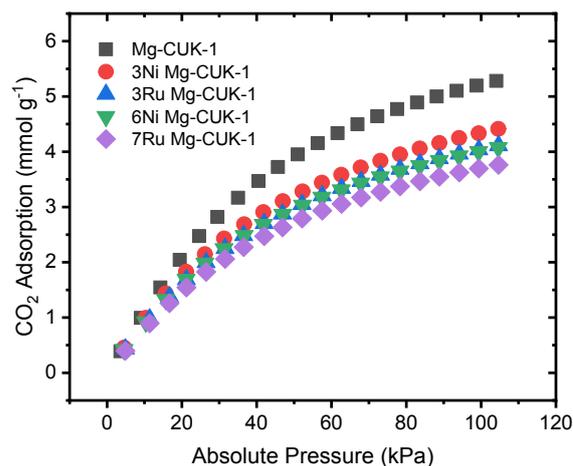


Figure 2. CO₂ adsorption isotherms of Mg-CUK-1, Ni-loaded Mg-CUK-1 and Ru-loaded Mg-CUK-1 conducted at 0 °C.

N₂ adsorption/desorption isotherms depict a similar trend in accessible surface area to the CO₂ uptake profiles (Figure S2). Mg-CUK-1 possessed the largest specific surface area of 542.3 ± 4.4 m² g⁻¹. 3Ni- and 3Ru-loaded Mg-CUK-1 registered a decrease in surface area to 389.7 ± 4.1 m² g⁻¹ and 386.7 ± 7.5 m² g⁻¹, respectively. Once the catalyst loading was increased further, the specific surface area again diminished to 365.9 ± 3.8 for 6Ni and 360.1 ± 7.0 for 7Ru. The slightly lower accessible surface area for Ru-loaded Mg-CUK-1 is attributed to the marginally higher catalyst loadings than Ni (Table S1).

From the CO₂ adsorption experiments, it's apparent that catalyst loading impacts CO₂ uptake. Increased catalyst loadings result in a decrease in both specific surface area and CO₂ adsorption capacity. Therefore, when considering combined carbon capture and utilisation hybrid sorbent/catalysts, minimizing the catalyst loading is preferential from a carbon capture point of view, so long as the catalytic activity is sufficient to convert all the captured CO₂. The following section will assess the performance of each material for CO₂ hydrogenation.

3.3 CO₂ Hydrogenation Catalyst Performance

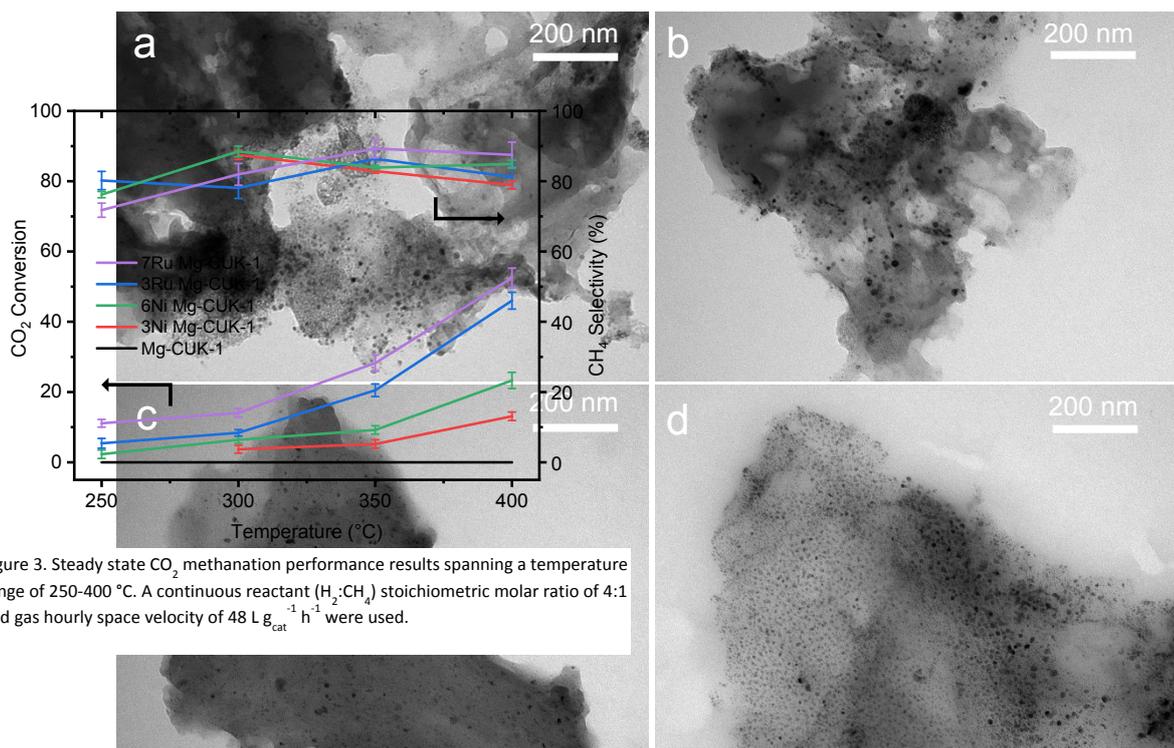


Figure 3. Steady state CO_2 methanation performance results spanning a temperature range of 250–400 °C. A continuous reactant (H_2 : CH_4) stoichiometric molar ratio of 4:1 and gas hourly space velocity of $48 \text{ L g}_{\text{cat}}^{-1} \text{ h}^{-1}$ were used.

Figure 4. Transmission electron micrographs of a) 3Ni, b) 6Ni, c) 3Ru and d) 7Ru-loaded Mg-CUK-1 indicating variations in nanoparticle dispersion and morphology.

The CO_2 hydrogenation performance of catalyst-loaded Mg-CUK-1 was assessed across a series (250–400 °C) of reaction temperatures under a steady-state stoichiometric flow of H_2 and CO_2 (4:1) (Figure 3, Table S2). CO_2 conversion was detected from 250 °C for all catalysts (6Ni, 3Ru and 7Ru) except 3Ni, which registered catalytic activity beyond 300 °C. An increase in CO_2 conversion was observed for all catalysts with increasing temperature. Ru-loaded materials outperformed Ni at comparable loadings throughout the observed temperature range. Similarly, higher loadings led to improved CO_2 conversion for both Ru and Ni. No catalytic activity was observed for samples containing only Mg-CUK-1, highlighting the importance of the Ru and Ni nanocatalysts in facilitating CO_2 conversion.

All catalysts demonstrate selectivity for CH_4 over CO , ranging between $71.8 \pm 2.0\%$ and $88.9 \pm 1.1\%$. Ru-Mg-CUK-1 offered the highest CH_4 selectivity at 350 °C, reaching $86.4 \pm 2.8\%$ and $89.3 \pm 2.6\%$ for 3Ru and 7Ru, respectively. Ni-loaded Mg-CUK-1 registered a maximum CH_4 selectivity at 300 °C, recording $87.5 \pm 1.3\%$ and $88.5 \pm 1.5\%$ for 3Ni and 6Ni, respectively.

The largest disparity in catalyst activity occurred at 400 °C, where 3Ru and 7Ru reached CO_2 conversions of $46.0 \pm 2.4\%$ and $52.5 \pm 2.8\%$, respectively. Conversely, 3Ni and 6Ni reached a maximum CO_2 conversion of $13.1 \pm 1.2\%$ and $23.3 \pm 1.3\%$, respectively.

To understand variations in catalytic performance between each hybrid sorbent/catalyst, transmission electron microscopy was conducted to provide insights into nanoparticle dispersion and morphology (Figure 4). Ni-loaded Mg-CUK-1 revealed a broader size distribution of nanoparticles than Ru at both catalyst loadings. Lower particle dispersion is also evident, with

regions of significant nanoparticle formation and regions completely absent of nanoparticles. Conversely, Ru-loaded Mg-CUK-1 appeared highly dispersed throughout the MOF crystals, even at the higher loading of 7 wt% Ru. Greater dispersion and narrower particle size distribution is likely a significant factor in the elevated catalytic performance of the Ru-loaded Mg-CUK-1 materials. The greater Ru dispersion may be due to the higher catalyst precursor solubility of $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ compared to NiCl_2 used during double solvent impregnation, allowing for greater transport within the hydrophilic MOF pores. X-ray diffraction of the spent Ni- and Ru-loaded Mg-CUK-1 highlight the retention of MOF crystallinity (Figure S3).

Based solely on the CO_2 hydrogenation performance results, Ru-loaded Mg-CUK-1 represents the superior catalyst with consistently higher CO_2 conversion and comparable CH_4 selectivity when evaluated against the Ni-loaded Mg-CUK-1. Higher loadings are also preferred, providing additional active sites to facilitate CO_2 hydrogenation.

However, the disparity in performance between catalysts is less pronounced when considering lower reaction temperatures. At 300 °C, 3Ru and 7Ru reach a CO_2 conversion of $8.4 \pm 0.9\%$ and $14.1 \pm 1.2\%$, respectively. 3Ni and 6Ni register a CO_2 conversion of $3.7 \pm 1.1\%$ and $6.4 \pm 1.0\%$, respectively. Given the strong contrast in operating conditions for steady-state CO_2 hydrogenation and a batch-mode temperature swing CO_2 capture and conversion scenario, where the reactor is repeatedly heated up to reaction temperature and cooled again to facilitate CO_2 adsorption, it is worthwhile assessing each hybrid sorbent/catalyst under relevant conditions before making a judgement on which material is best suited for a combined CO_2 capture and conversion system.

3.4 Influence of CO₂ stream composition on overall system performance

A series of temperature-swing batch mode performance tests were conducted to assess each material as a hybrid sorbent/catalyst for CO₂ capture and conversion (**Figure 5**). CO₂ adsorption was performed first at 25 °C allowing the sorbent to reach saturation over 60 min before raising the system to reaction temperature. The captured CO₂ was then desorbed and recirculated with H₂ for 20 min to enable the reaction. A reaction temperature of 300 °C was selected to minimise the system's energy footprint while offering a reasonable CO₂ conversion rate. A representative raw gas chromatograph – flame ionization detector signal for the hybrid sorbent/catalyst CO₂ capture and conversion experiments can be found in the supporting information (Figure S4).

A stream containing 100% CO₂ was first examined during the CO₂ capture operation to maximise the quantity adsorbed. The amount of CO₂ desorbed was inversely correlated to catalyst loading, with 3 Ni and 3Ru desorbing 3.48 and 3.51 mmol g⁻¹ while higher loadings of 6Ni and 7Ru desorbed 3.30 and 3.31 mmol CO₂ g⁻¹, respectively. These results corroborate what was observed in the CO₂ adsorption isotherms, where lower loadings afforded larger CO₂ uptakes (Figure 2).

The same CO₂ adsorption/desorption trend was observed when the feed CO₂ stream concentration was reduced. A feed concentration of 15% CO₂/N₂ was selected to emulate a typical post-combustion dry flue gas from a coal-fired or natural gas-fired power plant.⁴⁸ Again, 3Ni and 3Ru registered specific CO₂ desorption quantities of 1.39 and 1.40 mmol g⁻¹, respectively. The larger catalyst loadings of 6Ni and 7Ru resulted in slightly lower CO₂ desorption quantities of 1.31 and 1.32 mmol g⁻¹, respectively. All CO₂ desorption amounts for the 15% CO₂ feed are lower than observed for the 100% CO₂ feed stream. The effect is characteristic of adsorption-based CO₂ capture, where lower CO₂ partial pressures result in lower uptakes.³⁰ This is also reflected in the CO₂ adsorption isotherms for each material (Figure 2).

From a reaction perspective, the amount of CO₂ desorbed closely matched the quantity of CH₄ generated for all materials. This indicates that all the CO₂ initially adsorbed was able to be desorbed under reaction conditions. Furthermore, each hybrid sorbent/catalyst possessed sufficient catalyst loading to facilitate the complete conversion to methane. No CO was

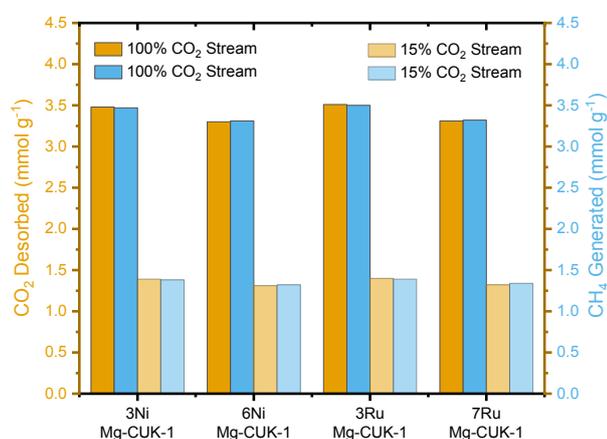


Figure 5. CO₂ capture and conversion batch recirculation results. Orange and blue columns denote CO₂ desorbed and CH₄ generated, respectively. Solid and transparent columns denote 100% and 15% CO₂ stream composition during CO₂ adsorption at 25 °C.

observed in these batch recirculation experiments, which is distinct from what was seen in the steady state CO₂ hydrogenation performance tests. The difference in performance can be attributed to the longer effective residence time for the reaction to occur during batch recirculation and the excess of H₂ present compared with the stoichiometric ratio (4:1) used under continuous CO₂:H₂ flow. Complete conversion to CH₄ is advantageous in real-world settings, reducing the need for further downstream gas separations before transport and end-use.

The batch performance results offer insights into key features when designing hybrid sorbent/catalyst materials. CO₂ capture, particularly from dilute CO₂ streams, represents the rate-determining step of the overall process. In the system discussed here, 60 min of 15% CO₂ flow was required to reach sorbent saturation, while complete conversion to CH₄ took less than 20 min. Once the system was switched to recirculation, the quantity of CH₄ generated was constrained by the amount of CO₂ captured by the sorbent initially. Therefore, maximising the CO₂ adsorption capacity of the included sorbent while minimizing the amount of catalyst represents a critical hybrid material design consideration. Minimizing catalyst loading allows for the maximum CO₂ adsorption capacity within the selected sorbent. However, maintaining enough catalyst to facilitate the complete conversion of captured CO₂ is required. In this case, 3Ni and 3Ru provide enough activity to convert all the CO₂ captured initially by the Mg-CUK-1 sorbent. Higher loadings (6Ni and 7Ru) decrease overall system performance caused by diminished CO₂ uptake.

3.5 Effect of oxygen exposure on recycled catalyst performance

Another important consideration in designing hybrid sorbent/catalysts is the resilience of the included catalyst towards oxygen exposure. Oxygen is present in CO₂-rich point source emissions arising from fossil fuel power generation, cement production and ethanol fermentation as well as direct air capture scenarios.

To assess catalyst oxygen tolerance, 3 wt% Ni and 3 wt% Ru underwent ten repeated CO₂ capture and conversion batch performance tests (**Figure 6**). The hybrid sorbent/catalyst was exposed to a 15% CO₂ in an 85% air stream throughout the carbon capture operating mode. 3Ru maintained CH₄ generation between 1.39 and 1.41 mmol g⁻¹ over the ten cycles, demonstrating resilience towards oxygen exposure. In contrast, 3Ni registered an 11.4% decrease in CH₄ generation from an initial value of 1.40 mmol g⁻¹ to 1.24 mmol g⁻¹ after ten cycles. The reduction in CH₄ generated resulted from incomplete CO₂ conversion, with unreacted CO₂ observed in the gas chromatographs.

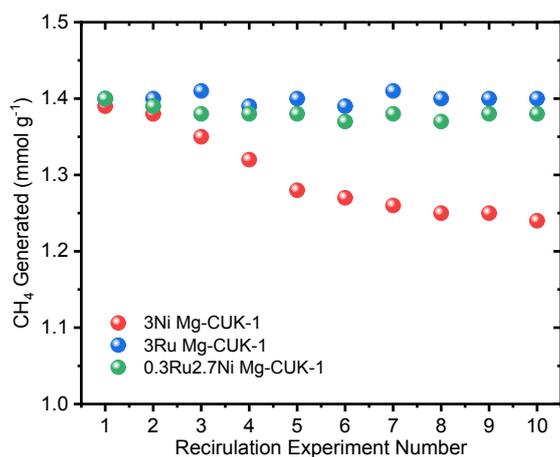


Figure 6. Influence of the included metal nanoparticle on catalyst performance upon exposure to air during CO₂ capture.

To improve the oxygen tolerance of 3Ni, a RuNi mixed metal catalyst was loaded onto Mg-CUK-1. The resulting hybrid 0.3Ru2.7Ni sorbent/catalyst contained 0.34 wt% Ru and 2.73 wt% Ni (Table S1). XRD and CO₂ adsorption isotherms can be found in the supporting information (Figures S5–S6). Upon exposure to ten repeated capture and conversion performance tests, 0.3Ru2.7Ni maintained a CH₄ generation of between 1.40 and 1.37 mmol g⁻¹.

To understand the retained performance observed in 0.3Ru2.7Ni, XPS was conducted on each material before and after the oxygen-tolerance performance tests (Figures S7–S8). Before catalytic performance testing, both 3Ni and 0.3Ru2.7Ni contained spin-orbit splitting peaks within the Ni 2p region at binding energies of 872.51 eV (2p_{1/2}) and 853.4833 eV (2p_{3/2}), indicating Ni²⁺ reduction to Ni⁰ (Figure 7). After ten reaction cycles, peaks associated with Ni⁰ were not observable in the spent 3Ni, while more Ni⁰ was retained within 0.3Ru2.7Ni. The XPS observations suggest that Ni oxidation was responsible for diminished catalyst performance within 3Ni, while 0.3Ru2.7Ni retained more active Ni⁰ species to facilitate CO₂ hydrogenation. A persistent set of spin-orbit splitting peaks at binding energies of 873.64 eV (2p_{1/2}) and 855.50 eV (2p_{3/2}) were evident throughout all samples, indicating a degree of oxidation (as NiO or Ni(OH)₂) present, likely due to atmospheric exposure during handling before measurement.

While quantification of the Ni²⁺ to Ni⁰ ratio is challenging given the complexity of Ni 2p XPS spectra, it is possible to qualitatively compare Ni 2p_{3/2} peaks to assess the extent of Ni reduction maintained after performance testing (Tables S3–S5).⁴⁹ The deconvoluted peaks at ~853 eV and ~855 eV offer an approximation to the relative quantities of surface Ni⁰ and Ni²⁺ present within each sample. Before cyclic performance testing, 3Ni and 0.3Ru2.7Ni possessed similar degrees of oxidation corresponding to 27.1% and 28.1% Ni⁰ relative to Ni²⁺. After oxygen tolerance performance testing, 3Ni relinquished the peak corresponding to Ni⁰, indicating complete Ni oxidation, while 0.3Ru2.7Ni retained 23.6% Ni⁰ relative to Ni²⁺. These semi-quantitative results highlight that the presence of Ru within a Ni-dominant hybrid sorbent-catalyst coincided with

greater retention of active Ni⁰ species after repeated oxygen exposure.

XPS regions corresponding to Ru were also analyzed to gain similar insights found for Ni. Unfortunately, the strong overlap in Ru 3d and C 1s peaks made it difficult to assess the degree of Ru oxidation in 3Ru and 0.3Ru2.7Ni (Figure S9).⁵⁰ Ru peak intensities were dwarfed by the much higher concentration of C present within the 2,4-pyridine dicarboxylate organic linker of Mg-CUK-1. Nevertheless, Ru 3d peaks were observed for the neat 3Ru at binding energies of 281.06 eV and 282.49 eV, likely corresponding to RuO₂ species. After oxygen tolerance performance testing, a shift to lower binding energies (280.97 eV and 282.37 eV) indicated a decrease in the Ru oxidation state. Complementary peaks for Ru 3p were also observed for 3Ru; however, the low Ru loading of 0.3Ru2.7Ni precluded any observable peak within the Ru 3p region (Figure S10). A Ru3p_{3/2} peak shift from 463.20 eV (3Ru Neat) to 462.90 eV (3Ru Spent) indicated a decrease in Ru oxidation state towards active Ru⁰ species after oxygen tolerance performance testing. The retention of Ru⁰ species appears pivotal to the enduring catalytic performance of 3Ru Mg-CUK-1 despite oxygen exposure during CO₂ capture.

The Mg coordination environment within Mg-CUK-1 changed upon catalyst loading and performance testing. A dominant peak centered at 49.71 eV within the Mg 2p region was observed for neat Mg-CUK-1 (Figure S11). After catalyst loading, the peak center shifted to 50.45 eV, 50.65 eV and 50.46 eV for 3Ni, 3Ru and 0.3Ru2.7Ni, respectively. The spent samples containing Ru indicated a reversion in binding energy back towards the neat Mg-CUK-1, with peaks centered at 50.50 eV and 50.35 eV for 3Ru and 0.3Ru2.7Ni, respectively. The subtle shift to lower binding energies alludes to a shift in electron density from Mg–O coordination bonds present within Mg-CUK-1 towards Mg–OH moieties lining the MOF interior.⁵¹ 3Ni continued to shift the Mg 2p peak to higher binding energy (50.53 eV) after performance testing. The varied trend in the Mg coordination environment may be caused by the difference in redox properties between Ru and Ni.

The O 1s region for Mg-CUK-1 revealed a dominant peak centered at 531.64 eV with lower intensity peaks on either side at 529.47 eV and 533.33 eV (Figure S12). Upon catalyst loading, the peak centered at 531 eV became dominant, likely due to the inclusion of Ru–O and Ni–O surface species. The spent materials

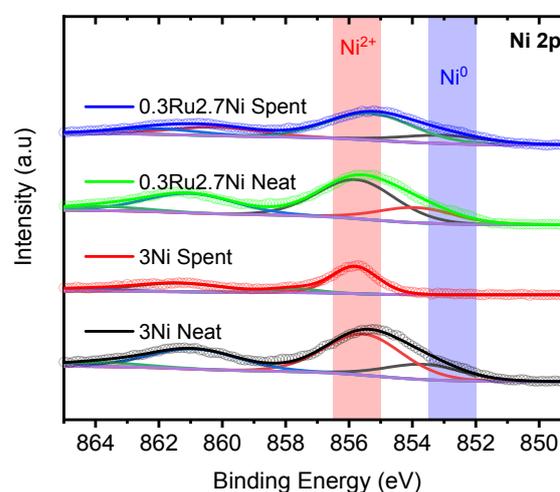


Figure 7. High-resolution X-ray photoelectron spectroscopy of 3Ni, and 0.3Ru2.7Ni before and after 10 carbon capture and conversion performance tests.

retained a similar oxygen coordination environment to the Ni- and Ru-loaded Mg-CUK-1. Given the large variety of oxygen bonding in both Mg-CUK-1 and the oxidized catalysts, it is difficult to glean much insight from the O 1s region.

The N 1s region reveals that the nitrogen in 2,4-pyridine dicarboxylate was retained upon catalyst loading and performance testing (Figure S13). Given that the Mg-N coordination bond represents the weakest junction within Mg-CUK-1, the persistent nitrogen coordination environment is a testament to the stability of the Mg-MOF under harsh reaction conditions. Similarly, C 1s peaks associated with Mg-CUK-1 remain consistent throughout catalyst loading and performance testing (Figure S9). Graphitic carbon generation associated with MOF decomposition previously seen with Mg-MOF-74 is not observed for Mg-CUK-1.³⁸ Catalyst dispersion (Figure S14) appears similar in 0.3Ru2.7Ni to what was observed in Figure 4.

Several studies involving Ni-based hybrid sorbent/catalysts have been conducted previously; however, they primarily involve O₂-free CO₂ streams.^{11, 52-54} The surface passivation of Ni active sites has been observed elsewhere, indicating its lack of suitability for hybrid sorbent/catalyst systems involving exposure to O₂.²⁸

Conversely, Ru possesses distinctive redox properties that allow for rapid reduction after exposure to O₂.^{12, 27} PGMs, such as Ru, are known to dissociate H₂, providing a strong reducing agent (H[•] radicals) to lower the reduction temperature required for NiO.⁵⁵ Therefore, by introducing small quantities of Ru into a predominantly Ni-based catalyst, the hybrid sorbent/catalyst's overall performance can be sustained without relying solely on PGMs. The economic implications of utilising Ru-based catalysts at scale are worth considering. As of May 2022, Ru (\$US22.7/g) was almost three orders of magnitude more expensive than Ni (\$US 0.03/g). If Ni can replace a significant portion of the Ru used within a hybrid sorbent/catalyst, this can translate to a significant operating cost reduction when considering carbon capture and conversion industrial implementation. Ru-promoted Ni nanocatalysts can facilitate the re-reduction of surface NiO species such that both Ni and Ru sites remain active for CO₂ hydrogenation.⁵⁶ However, using low loadings of Ru (0.5%Ru) in the absence of Ni has led to diminished performance upon cycling, attributed to deactivation and potentially sintering upon exposure to O₂ and steam in flue gas.²⁰

3.6 Comparison of hybrid sorbent/catalyst performance with previously reported dual functional materials

The overall hybrid sorbent/catalyst performance of 0.3Ru2.7Ni Mg-CUK- is closely associated with the CO₂ adsorption behaviour exhibited by Mg-CUK-1. A promising CO₂ adsorption capacity (1.4 mmol g⁻¹ with 15% CO₂/air flow) relative to most of the previously reported metal oxide/carbonate-based DFMs provides a platform for enhanced CH₄ generation. A summary of previously reported DFM performance data for the capture and conversion of CO₂ to CH₄ can be found in the supporting information (Figure S15 and Table S6). Most experimental studies in the literature involving DFMs utilize an isothermal reactor configuration, different to

the temperature-swing reactor operating conditions used in this work. The key experimental conditions associated with each previously reported study used for comparison are tabulated in Table S6.

Weak-to-moderate CO₂ interactions within Mg-CUK-1 allow for complete CO₂ desorption well below hydrogenation reaction temperature. Consequently, all the CO₂ captured originally is released and available for CH₄ generation. Complete CO₂ release is not always a feature of hybrid sorbent/catalysts using metal oxides.²⁴ Upon forming carbonate or bicarbonate species, the temperatures required for complete chemical sorbent regeneration may exceed the required hydrogenation reaction temperature. This is most notable for DFMs reliant on CaO or MgO for CO₂ uptake. If a low reaction temperature (such as 300 °C) is selected, incomplete CO₂ desorption is likely, resulting in a reduced sorbent working capacity. The work presented here allows for complete CO₂ desorption and conversion to CH₄ at 300 °C.

Utilising solid adsorbents with large CO₂ uptakes and low regeneration temperatures is central to designing hybrid sorbent/catalysts for combined CO₂ capture and conversion applications. Highly dispersed nanocatalysts at low loadings allow for greater preservation of CO₂ adsorption capacity. The chosen catalyst needs to be able to withstand exposure to reactive species such as oxygen that are often present in CO₂-rich point source emissions. In this work, Ni-based catalysts were unable to retain their performance after oxygen exposure. However, once combined with a small loading of Ru (0.34 wt%), the Ni species retained their catalytic activity. Future work will assess the feasibility of applying hybrid sorbent/catalysts to direct air CO₂ capture and conversion to chemical fuels. Further material design and engineering optimisation will also be conducted to tailor the system to more challenging CO₂ capture streams that include other reactive species such as H₂O, NO_x and SO₂.

4 Conclusions

The advancement of hybrid sorbent/catalysts for the combined capture and conversion of CO₂ to CH₄ requires an understanding into how both the selected sorbent and catalyst perform under industrially relevant conditions. Sorbents capable of large CO₂ adsorption capacities through weak-to-moderate interactions allow for complete CO₂ utilisation at mild reaction temperatures. Mg-CUK-1 exhibits a physisorption-driven CO₂ uptake of 1.40 mmol g⁻¹ under simulated dry flue gas conditions. CO₂ capture was identified as the limiting factor in overall system performance. By minimizing catalyst loading to 3 wt%, most of the CO₂ uptake within Mg-CUK-1 is preserved without compromising subsequent catalytic hydrogenation to CH₄.

The selected catalyst must withstand O₂ exposure during CO₂ capture when considering real-world point source CO₂ emissions. Ru nanoparticles (3Ru Mg-CUK-1) were capable of withstanding oxygen exposure resulting in the sustained catalytic performance of 1.40 mmol CH₄ g⁻¹ over ten carbon capture and conversion cycles. In contrast, Ni nanoparticles (3Ni Mg-CUK-1) could not maintain initial catalytic performance,

resulting in an 11.4% decrease in CH₄ generation over ten cycles.

When a small amount of Ru was added to Ni Mg-CUK-1, the resulting hybrid sorbent/catalyst (0.3Ru2.7Ni Mg-CUK-1) retained catalytic performance despite oxygen exposure during CO₂ capture. Including 0.3 wt% Ru into a predominantly Ni-based catalyst (0.3Ru2.7Ni Mg-CUK-1) enables equivalent hybrid sorbent/catalyst performance to 3Ru Mg-CUK-1. The finding helps reduce the cost of hybrid sorbent/catalyst systems without compromising overall performance. The demonstrated material design approach can be used to establish more resilient catalysts in the presence of a range of reactive species known to diminish performance.

Author Contributions

TZ contributed to the conceptualization, formal analysis, investigation, methodology, visualization, and writing – original draft. KL, ZH, JS and RA assisted with the conceptualization, project administration, supervision, and writing – review & editing. JS and EL aided the methodology development. JS and RA facilitated the funding acquisition.

Conflicts of interest

The authors have no conflicts of interest to declare.

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