

Contents lists available at ScienceDirect

Separation and Purification Technology



journal homepage: www.elsevier.com/locate/seppur

Ni/support-CaO bifunctional combined materials for integrated CO₂ capture and reverse water-gas shift reaction: Influence of different supports

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ARTICLE INFO

Integrated CO2 capture and utilisation

Reverse water-gas shift reaction

Bifunctional combined materials

Keywords:

ABSTRACT

Integrated CO₂ capture and utilisation (ICCU) is a promising strategy for restricting carbon emissions and achieving carbon neutrality. Bifunctional combined materials (BCMs), containing adsorbents and active catalysts, are widely applied in this process. Producing syngas via reverse water-gas shift reaction (RWGS) and integrating with Fischer-Tropsch (F-T) synthesis is an attractive and valuable CO₂ utilisation route. This work investigated a series of Ni/support-CaO BCMs (supports = ZrO₂, TiO₂, CeO₂ and Al₂O₃) for the integrated CO₂ capture and RWGS (ICCU-RWGS) process. The Ni/support-CaO BCMs were prepared by physically mixing various metal oxide supports loaded Ni with sol-gel derived CaO. The ICCU-RWGS performance (CO2 conversion, CO yield and CO generation rate) of these BCMs followed the order during tested conditions (550-750 °C): Ni/ CeO2-CaO > Ni/TiO2-CaO > Ni/ZrO2-CaO > Ni/Al2O3-CaO. A comprehensive characterisation of Ni/support materials showed that Ni/CeO₂ had the characteristics of stronger basicity, optimal Ni dispersion and improved NiO reducibility, which led to the outperforming ICCU-RWGS activity over Ni/CeO2-CaO (e.g. 56.1% CO2 conversion, 2.68 mmol g⁻¹ CO yield and ~100% CO selectivity at 650 °C). Furthermore, the Ni/CeO₂-CaO BCM showed a stable, yet, self-optimising catalytic performance during the cyclic ICCU-RWGS reaction over 20 cycles. The TEM characterisation suggested that was ascribed to the volume expansion and shrinkage of CaO in the cyclic adsorption-desorption altering the distance between the adsorbent and Ni/CeO2, resulting in an enhanced CO₂ conversion during the cycle.

1. Introduction

With the wide use of fossil fuels, a substantial amount of CO_2 emissions is emitted into the atmosphere, leading to severe environmental issues [1], such as sea level rise [2], ocean acidification [3] and extreme weather [4]. In order to reduce industrial carbon emissions, CO_2 capture is one of the most promising techniques and has attached a lot of attention [5–8]. Currently, the most mature CO_2 capture technologies are solvents adsorption (i.e. MEA) [9] and calcium looping [10–13], which are both operated by swinging temperature to regenerate the adsorbents. The obtained high concentration of CO_2 could be stored by deep-sea injection or mineralisation [14], which is known as carbon capture and storage (CCS). However, the CCS requests a high capital

investment and may not be a long-term sustainable solution due to the risk of the second release of stored CO_2 [15]. Therefore, there is an increasing interest in the direct utilisation of the captured CO_2 , which is known as integrated CO_2 capture and utilisation (ICCU).

The ICCU process can eliminate the CO₂ enrichment, storage and transportation steps by in-situ converting the captured CO₂ [16] and isothermally producing valuable products (e.g. CH₄ or CO [17–20]). In a typical ICCU process, CO₂ is first adsorbed on adsorbents (i.e. CaO), and then a reducing agent (i.e. H₂) is introduced to react with the captured CO₂ with the assistance of active catalytic sites. Among the final products of the ICCU process, carbon monoxide (CO) is considered to be one of the most valuable chemicals to be used as the feedstock for the mature Fischer-Tropsch process to further produce liquid products [21–23]. The

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https://doi.org/10.1016/j.seppur.2022.121604

Received 24 May 2022; Received in revised form 22 June 2022; Accepted 25 June 2022 Available online 28 June 2022

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commonly used CO_2 reduction technologies include thermal-catalysis, photo-catalysis, electro-catalysis, plasma-catalysis and etc. [24]. Thermal-catalyzed CO_2 reduction is a relatively compromised choice in terms of high process efficiency and low input cost (e.g. equipment investment and materials costs). The reverse water–gas shift (RWGS) reaction, as shown in Eq. (1), is a promising process for thermal catalytic conversion of CO_2 that uses renewable H_2 to reduce carbon emissions and produce syngas.

$$CO_2 + H_2 = CO + H_2O (1)$$

The bifunctional combined materials (BCMs), containing CO_2 adsorbent and active catalytic sites, have been proven effective for the ICCU process [20,23,25–27]. Specifically, CaO is widely used as high temperature CO₂ adsorbent [28,29], and Ni can act as catalytic sites for RWGS [30,31]. The previous study [32] has concluded that the physical mixing is a superior material preparation method by avoiding catalytic sites coverage due to CaO sintering. The supports of Ni-catalysts are widely believed to play key roles in the catalytic process owing to the metal dispersion, metal-support interaction, etc. [33–35]. However, as a novel process, ICCU provide CO_2 in the form of carbonates, which possesses different chemical environment than traditional RWGS. Therefore, there is a gap on understanding of the effects of supports in ICCU, including the effects on CO_2 adsorption and catalytic conversion.

In this work, to investigate the support effects on ICCU-RWGS, two active supports (CeO₂ and TiO₂) and inert materials (ZrO₂ and Al₂O₃) supported Ni are synthesised as catalysts, and a sol–gel prepared CaO as the adsorbent to prepare the BCMs. The sol–gel CaO has been proven a stable and excellent CO₂ adsorbent in carbon capture [36]. The CeO₂ and TiO₂ have been widely applied to catalytic processes, including RWGS, CO₂ methanation, dry reforming etc. [37,38]. Furthermore, the active TiO₂ and inert Al₂O₃ could form spinel with Ni (strong metal-support interaction) [39,40], which provide valuable benchmarks for identifying active sites.

2. Experimental section

2.1. Bifunctional combined materials preparation

 $\rm ZrO_2$ (Sigma-Aldrich, 99%), TiO_2 (Sigma-Aldrich, 99.5%) and $\rm Al_2O_3$ (Sigma-Aldrich, 99.5%) were dried at 120 °C before the impregnation process. CeO₂ was prepared by a hydrothermal method as reported in previous work [17,19]. Briefly, 5.21 g Ce(NO₃)₃·6H₂O (Sigma-Aldrich, 99%) was dissolved in deionised water (30 ml) to prepare a Ce source solution, followed by the dissolution of 57.6 g NaOH (Sigma-Aldrich, 99%) in deionised water (210 ml) to prepare the precipitant. The Ce source was mixed with the precipitant dropwise for 30 mins at room temperature to obtain a slurry. The slurry was transferred into a stainless-steel autoclave and kept at 100 °C for 24 h. The precipitate was washed and separated by vacuum filtration using distilled water and ethanol to neutrality and dried at 120 °C overnight, to produce a yellow powder, labeled as CeO₂. Ni-based catalysts were prepared by the wet impregnation method, using Ni(NO₃)₂·6H₂O (Sigma-Aldrich, 97%) as the metal precursor. Typically, 3.0 g support material was added into 30 ml Ni(NO₃)₂ (0.15 mol L⁻¹) aqueous solution, stirred at room temperature for 2 h and evaporated under stirring to produce a sample paste. The sample paste was dried at 120 °C overnight, and calcined at 800 °C for 5 h with a heating rate of 5 °C min⁻¹, to produce NiO/ZrO₂, $\rm NiO/TiO_2,\ NiO/CeO_2$ and $\rm NiO/Al_2O_3,\ respectively.$ The NiO/supports were reduced at 550 °C for 2 h with a heating rate of 5 °C min⁻¹ in 5% H₂/N₂, and labeled as Ni/ZrO₂, Ni/TiO₂, Ni/CeO₂ and Ni/Al₂O₃, respectively.

The sol-gel derived CaO was prepared as reported in previous work [20,32]. Briefly, 23.6 g Ca(NO₃)₂·4H₂O (Sigma-Aldrich, 99%) and 19.2 g citric acid monohydrate (Sigma-Aldrich, 99.5%) were dissolved into 72 ml distilled water, stirred at room temperature at 80 °C, and dried at 120 °C overnight. The sample was ground and calcined at

850 °C for 5 h with a heating rate of 5 °C min⁻¹, labeled as sol–gel CaO. The bifunctional combined materials were prepared by physically mixing the Ni/support catalysts and the sol–gel CaO with a mass ratio of 1:2, labeled as Ni/ZrO₂-CaO, Ni/TiO₂-CaO, Ni/CeO₂-CaO and Ni/Al₂O₃-CaO, respectively.

2.2. Materials characterisation

The loadings of Ni on various supports were measured by inductively coupled plasma-optical emission spectroscopy (ICP-OES). The samples were digested in nitric acid and then analysed using a Perkin Elmer PE2400 CHNS. X-ray diffraction (XRD) patterns (2 Theta: 5°-75°) were measured by a PANalytical Empyrean Series 2 diffractometer with a Cu Ka X-ray source. The surface area and pore structure of the Ni/supports catalysts were characterised by an ASAP 3000 analyser at 77 K. The Brunauer-Emmett-Teller (BET) method and the desorption isotherm branch were applied to calculate the surface area and the pore size distribution, respectively. The X-ray photoelectron spectrum (XPS) analysis was performed on a Thermo Fisher Scientific NEXSA spectrometer. H₂ temperature-programmed reduction (H₂-TPR) of the NiO/ support catalysts was tested on a Hi-Res TGA 2950 thermogravimetric analyser. Typically, the samples were pre-treated under N₂ at 300 °C for 30 mins to remove the adsorbed H₂O and gases, equilibrated to 50 °C and temperature programmed reduced in 100 ml min⁻¹ 5% H₂/N₂ (10 °C/min to 800 °C). The CO₂ temperature-programmed desorption (CO2-TPD) patterns of the Ni/support catalysts were measured by a Micromeritics Autochem II 2920 analyser. The Ni/support catalysts were in-situ reduced at 550 °C in H2 for 1 h and then cooled down to 30 °C in He. After adsorbing CO₂ at 30 °C in 10% CO₂/He, the temperature was increased to 800 °C in He with a heating rate of 10 °C min⁻¹. Scanning electron microscopy coupled with an energy dispersive X-ray spectrometer (SEM-EDX, FEI Quanta FEG) was used to characterise the morphology and element dispersion. Transmission electron microscopy (TEM, FEI Titan3 Themis 300) and high-angle annular dark-field transmission electron microscopy (HAADF-TEM) were utilised to observe the morphology and Ni particle size of Ni/ support catalysts. The Ni particle size distribution was calculated from TEM observation.

2.3. Integrated CO₂ capture and RWGS (ICCU-RWGS) evaluation studies

The ICCU-RWGS evaluations of Ni/support-CaO were carried out in a fixed-bed reactor and monitored by an online gas analyser (Kane Autoplus 5). The stainless-steel reaction tube (length: 500 mm, inner diameter: 64 mm) was placed in the middle of the tube furnace (Elite TSH-2416CG). Briefly, 0.30 g Ni/support-CaO bifunctional combined materials (BCMs) were placed in the middle of the reaction tube and fixed in place by quartz wool. Two thermocouples were placed in the reaction tube and inside the tube furnace to monitor the temperature of the BCMs and tube furnace, respectively.

In a typical evaluation test, the BCMs were reduced at 550 °C in 5% H_2/N_2 for 2 h, and then the gas was switched to 100 ml min⁻¹ 20% CO₂/ N_2 for ~28 mins. 100 ml min⁻¹ 5% H_2/N_2 was then introduced for ~28 mins for the RWGS. Then the flowing gas was switched to N_2 and equilibrated the temperature for the following test. The baseline of carbonation and hydrogenation steps was monitored using 0.3 g SiO₂ to eliminate the analyser signal delay. The CO₂ conversion, CO yield and selectivity were calculated by integrating the real-time data collected from the online gas analyser from 0 s to 1700 s, referring to the equations below.

$$C_{CO2} = \frac{\int_0^{1700} (CO + CH_4)}{\int_0^{1700} (CO + CH_4 + CO_2)} *\%$$
(2)

Table 1

Summary of elem	ent analysis, BET,	pore size and a	average Ni cı	vstallite size.
			()	

Sample	Ni content ^a (wt. %)	S _{BET} ^b (m ² g ⁻¹)	V_{pore}^{c} (m ³ g ⁻¹)	Average pore size (nm)	Ni crystallite size ^d (nm)
Ni/ZrO ₂	7.8	4.7	0.1	21.1	34.1
Ni/TiO ₂	9.5	3.5	0.1	23.7	27.9
Ni/ CeO ₂	6.8	63.9	0.3	17.7	18.7
Ni/ Al ₂ O ₃	8.1	126.3	0.2	5.1	21.3
Sol-gel CaO	-	9.4	0.1	35.9	-

^a Element percentage evaluated by elemental analysis.

^b Multipoint BET surface area.

^c BJH method cumulative desorption pore volume.

^d Average Ni crystallite sizes calculated from XRD.

$$S_{CO} = \frac{\int_0^{1700} CO}{\int_0^{1700} (CO + CH_4)} *\%$$
(3)

$$Y_{CO} = \frac{\int_0^{1700} CO(\%^*s) * 1.667(ml/s)}{22.4(ml/mmol) * 0.30(g)}$$
(4)

 C_{CO2} , S_{CO} and Y_{CO} represent to CO_2 conversion (%), CO selectivity (%) and CO yield (mmol $g_{material}^{-1}$).

3. Results and discussion

3.1. Characterisation of Ni/support catalysts and Ni/support-CaO bifunctional combined materials

3.1.1. Ni/support catalysts

The elemental analysis of the Ni/support catalysts using inductively coupled plasma (ICP) showed that the Ni loadings on the various supports were controlled at 8 \pm 1.5 wt% (Table 1). N₂ isothermal adsorption–desorption was carried out to characterise the surface area and pore structure of the Ni/support materials (Fig. 1). As summarised in Table 1, the Ni/ZrO₂ and Ni/TiO₂ showed poor porosity with low BET surface areas (< 5 m² g⁻¹). In contrast, the Ni/CeO₂ and Ni/Al₂O₃ were more porous and possessed typical type IV isotherms with distinct hysteresis loops. As shown in Fig. 1, the Ni/CeO₂ and Ni/Al₂O₃ exhibited type H₃ and H₄ hysteresis loops with various pore size distribution. The pore size of Ni/CeO₂ and Ni/Al₂O₃ are ~10–40 nm and 3–10 nm, respectively. It

can also be demonstrated from TEM observation (Fig. 2i) that Ni/CeO_2 could accumulate slit-shaped pores with regular rod-like morphology. The higher surface area and porous structure could contribute to the dispersion of metals and the diffusion of reactants in catalytic reactions.

High-angle annular dark-field transmission electron microscopy (HAADF-TEM) was carried out to observe the dispersion of Ni species and the morphologies of the Ni/support catalysts. As shown in Fig. 2, all the Ni/support catalysts possessed gaussian distribution of Ni species size, following the decreasing order: Ni/TiO₂ > Ni/ZrO₂ > Ni/Al₂O₃ > Ni/CeO₂. The Ni species size distribution and the average Ni size are presented in Fig. 2d, h, l, p. The CeO₂ and Al₂O₃ can disperse Ni better than other supports, which is attributed to the morphology and porosity of supports. Specifically, the Ni/CeO₂ possesses the optimal Ni dispersion with a ~14.1 nm Ni species size.

The X-ray diffraction patterns of the Ni/support materials are presented in Fig. 3. Except for the amorphous Al_2O_3 supported Ni, all the other three samples showed distinct metallic Ni peaks (PDF#87-0712) and strong diffraction peaks which belong to the support materials, referring to ZrO_2 (PDF#86-1451), TiO_2 (PDF#75-1753) and CeO_2 (PDF#78-0694). In addition, the Ni/TiO_2 and Ni/Al_2O_3 catalysts exhibited NiTiO_3 (PDF#76-0334) and NiAl_2O_4 (PDF#77-1877) spinel peaks, respectively. There were no distinct NiO peaks, indicating that NiO was fully reduced at 550 °C during the reduction process. The reducibility of spinel is much poorer than NiO species [41,42], which could be verified by the presence of significant spinel peaks after reduction.

XPS was carried out, as shown in Fig. 4, to further confirm the valence state and chemical environment of surface nickel species of the reduced Ni/support catalysts. The Ni 2p3/2 XPS profiles of Ni/supports exhibit common peaks at ~852.1 eV and ~855.8 eV, which are attributed to the metallic Ni and its satellite peak, respectively [43]. The air contact could quickly oxidise surface metallic Ni, resulting in the existence Ni²⁺ peaks on the reduced Ni/support catalysts [44]. The multisplit peaks at 853.5-855.5 eV and 857-861 eV could be assigned as Ni²⁺ signals from NiO and their satellite peaks. Notably, there is no distinct NiO peaks on XRD characterisations (Fig. 3), indicating the oxidation only limitedly occurs on the surface of Ni. It is believed that the support interacted Ni would possess higher binding energy [45], which can be located at 856.5 eV and 862.3 eV. Notably, the Ni/Al₂O₃ possessed the most abundant metal-support interaction, indicating that the NiAl₂O₄ dominates on the surface of Ni/Al₂O₃ [39]. As a comparison, the surface NiTiO₃ could be effectively reduced and exhibited \sim 34% Ni⁰ even after air oxidation. It is noted that NiTiO₃ still dominate in bulk (Fig. 3), indicating that the Ni might parse out from NiTiO₃



Fig. 1. (a) N₂ adsorption-desorption isotherms; (b) Pore size distribution calculated from the BJH desorption branch.



Fig. 2. TEM, HAADF-mapping images and Ni size distribution of Ni/support catalysts. (Ni/ZrO₂: a, b, c and d; Ni/TiO₂: e, f, g and h; Ni/CeO₂: i, j, k and l; Ni/Al₂O₃: m, n, o and p).



Fig. 3. XRD patterns of Ni/support catalysts with various supports (ZrO_2 , TiO_2 , CeO_2 and Al_2O_3).

spinel and act as catalytic sites in ICCU. The Ni/CeO₂ exhibits lower metallic Ni fraction (18%) on the surface, attributed to the highly dispersed Ni, which could be easily reacted with O₂ in air.

The reducibility of the Ni species over the prepared NiO/support catalysts was further investigated by H₂-TPR, as shown in Fig. 5a. There are two reduction peaks over Ni/ZrO₂ and Ni/CeO₂ at 380–430 °C and 450–480 °C, which could be assigned as weakly and strongly interacted NiO species, respectively [41,46]. It is noted that the NiO/CeO₂ possessed the lowest reduction temperature, which is attributed to the smallest Ni particle size [47]. The spinel species (i.e. NiAl₂O₄ and NiTiO₃) formed during the high temperature calcination are more difficult to reduce, which is consistent with the XRD analysis. Specifically, the NiTiO₃ spinel can be reduced from ~600 °C and showed only one reduction peak at ~680 °C [41]. And there was no distinct reduction of Ni/Al₂O₃ in the TPR procedure [42]. The formation of spinel is believed to improve Ni dispersion [23],[48]; however, only the reducible Ni species are active catalytic sites.

 CO_2 -TPD profiles are presented in Fig. 5b to investigate the basicity of the Ni/support catalysts. Only Ni/CeO₂ and Ni/Al₂O₃ possessed CO₂



Fig. 4. XPS analysis of Ni 2p_{3/2} region of (a) Ni/ZrO₂; (b) Ni/TiO₂; (c) Ni/CeO₂ and (d) Ni/Al₂O₃.



Fig. 5. (a) H₂-TPR patterns of NiO/support catalysts and (b) CO₂-TPD patterns of Ni/support catalysts.

desorption peaks, which are attributed to their surface basic sites and superior porosity. The two desorption peaks of Ni/CeO₂ and Ni/Al₂O₃ at temperatures of < 100 °C and between 150 and 250 °C are attributed to weak and intermediate CO₂ chemisorption, respectively [49]. Ni/CeO₂ showed a higher CO₂ desorption temperature indicating that CeO₂ could provide stronger basic sites, which are beneficial for CO₂ adsorption and activation.

3.1.2. Ni/support-CaO bifunctional combined materials

The bifunctional combined materials (BCMs) for integrated CO_2 capture and reverse water–gas shift reaction (ICCU-RWGS) in this work were prepared by physically mixing the Ni/support catalysts and the

sol–gel prepared CaO. As shown in Fig. 6a, 6b and 6c, the images of SEM and TEM were applied to exhibit the morphologies of sol–gel CaO and fresh Ni/CeO₂-CaO BCM. The sol–gel CaO adsorbent possessed a spongelike structure with abundant large pores, consistent with the BET characterisation (Fig. 1 and Table 1). The porous structure could improve the CaO accessibility and prevent the severe sintering of CaO due to volume expansion during the carbonation process [36]. As shown in Fig. 6b, 6c and 6d, the physical mixing method could disperse Ni/CeO₂ into the sponge structure CaO, providing active sites near the adsorbent. In the previous research [32], the physical mixing method has been demonstrated to avoid the coverage of the catalytic sites caused by the volume expansion of CaO during the carbonation-hydrogenation ICCU process.



Fig. 6. SEM images of (a) fresh sol-gel CaO; (b) and (d) fresh Ni/CeO₂-CaO; (f) spent Ni/CeO₂-CaO; and TEM images of (c) fresh Ni/CeO₂-CaO and (e) spent Ni/CeO₂-CaO.

3.2. Integrated CO_2 capture and reverse water–gas shift reaction (ICCU-RWGS) performance

The ICCU-RWGS performance using Ni/support-CaO bifunctional combined materials (BCMs) with various supports (e.g. ZrO_2 , TiO_2 , CeO_2 and Al_2O_3) are shown in Fig. 7. Here Ni particles were used as active catalytic sites, and CaO played as the CO₂ adsorbent. A typical ICCU-RWGS process mainly included two steps, one was CO₂ adsorption from a diluted CO₂ source (e.g. 20% CO₂/N₂), and another was hydrogenation of the captured CO₂. The above two steps were isothermally operated by switching the inlet gas between 20% CO₂/N₂ and 5% H₂/N₂. The SiO₂/CaO was used as a blank benchmark material to demonstrate the ICCU-RWGS performance with bare inert support compared to active Ni metal over active supports. To reveal the optimal support for the ICCU-RWGS process, various Ni/support-CaO bifunctional combined materials were evaluated at 550–750 °C.

As shown in Fig. 7a and 7c, the CO₂ conversions and CO yields of

various Ni/support-CaO BCMs followed the decreasing order: Ni/CeO₂-CaO > Ni/TiO₂-CaO > Ni/ZrO₂-CaO > Ni/Al₂O₃-CaO. All of the Ni/support-CaO BCMs exhibited excellent CO selectivity (~100%) over the investigated temperature range. The Ni/Al₂O₃-CaO showed only a comparable performance with SiO₂-CaO in terms of CO₂ conversion and CO yield, indicating the poor catalytic activities of nonreducible NiAl₂O₄ spinel (Fig. 5a). However, Ni/TiO₂-CaO with NiTiO₃ spinel achieved much high CO₂ conversion compared to Ni/Al₂O₃-CaO owing to the better spinel reducibility. Although there was no spinel formation, Ni/CeO₂-CaO outperforms Ni/ZrO₂-CaO in relation to CO₂ conversion and CO yield. For example, Ni/CeO₂-CaO and Ni/ZrO₂-CaO achieved 56.1% and 34.0% for CO₂ conversion and 2.7 and 1.1 mmol g⁻¹ for CO yield at 650 °C, respectively.

The performances of ICCU-RWGS were also significantly affected by the reaction temperature. For example, 87.4% and 25.6% of CO₂ conversions were obtained over Ni/CeO₂-CaO at 550 °C and 750 °C, respectively. As an endothermic reaction, RWGS favors a higher reaction



Fig. 7. Integrated CO_2 capture and RWGS performance of various Ni/support-CaO BCMs: (a) CO_2 conversion; (b) CO selectivity; (c) CO yield and (d) C1 species ($CO_2 + CO + CH_4$) yield.

temperature which is consistent with the decomposition of CaCO₃. However, the fast decomposition of CaCO₃ could increase the CO₂ concentration near the catalytic sites resulting in a decrease in CO₂ conversion.

It is necessary to monitor the real-time ICCU-RWGS process to evaluate the CO₂ adsorption performance and catalytic activity. The promotion effect of support of Ni could be clearly demonstrated in the CO₂ adsorption stage, presenting as the enhanced CO₂ capture rate compared to the benchmark (SiO₂ line in Fig. 8a). Specifically, Ni/CeO₂-CaO and Ni/Al₂O₃-CaO exhibited superior CO₂ capture rate and capacity (~9.58 and 9.31 mmol g-1 at 650 °C for ~28 min), which was attributed to the abundant basicity of Ni/CeO₂ and Ni/Al₂O₃, as indicated in Fig. 5b.

The various Ni/support-CaO BCMs also exhibited distinct CO generation rates and real-time CO₂ conversion during the hydrogenation step. As shown in Fig. 8b and 8c, the Ni/CeO₂-CaO BCM could achieve an optimal real-time CO₂ conversion (~60%) and CO generation rate (~1.7 μ mol s⁻¹g⁻¹) at 650 °C. The excellent Ni dispersion and stronger basicity of Ni/CeO₂ might contribute to the superior ICCU-RWGS performance. It is worth noting that Ni/TiO₂-CaO also exhibited outstanding real-time CO₂ conversion (~57%), which might be attributed to the slowly released Ni from easily reducible NiTiO₃ spinel species (Figs. 3 and 4) [50]. As a comparison, Ni/Al₂O₃ showed poorer catalytic activities, indicating that the nonreducible spinel (Figs. 3 and 4a) played poor catalytic performance in ICCU.

In this work, we focused on the initial 1500 s of CO_2 conversion to evaluate the real-time gas production in ICCU-RWGS. The CO_2

desorption is relatively fast in the initial stage of the hydrogenation step (0–500 s), especially under higher temperature (e.g. 700 °C), which directly limits the CO₂ conversion rate at this stage (as shown in Fig. 8e and 8f). Since only 5% H₂/N₂ was used in this work, excessive CO₂ release would decrease the ratio of H₂:CO₂ and affect the equilibrium of RWGS reaction. After the rapid decomposition of the surface layer of CaCO₃, the release of CO₂ and the performance of RWGS is gradually stabilised until the carbonates are thoroughly consumed.

The scaled-up preparation of Ni/supports-CaO BCM is critical for deploying the ICCU-RWGS in an industrial scale. The adsorbents (CaO) are expected to be obtained from limestones, representing a low-cost mineral (<30 dollars per ton (DPT)). The Ni/supports are comprised of earth-rich elements, such as CeO₂ (~1600 DPT), TiO₂ (~3300 DPT), Al₂O₃ (~350 DPT), ZrO₂ (~1000 DPT) and Ni precursor (Ni (NO₃)₂*xH₂O, ~4000 DPT). By impregnating Ni onto a support and physically mixing catalysts and CaO, the BCMs could be obtained with an expected cost of ~300–1000 DPT. Notably, although H₂ can be obtained from renewable energy, the cost would dominate in the ICCU-RWGS process. The development of low-cost hydrogen production will also be the key to the low-cost deployment of ICCU.

3.3. ICCU-RWGS cycle evaluation

The stability of Ni/CeO₂-CaO bifunctional combined material was presented by carrying out 20 cycles of ICCU-RWGS at 650 °C (Fig. 9). The Ni/CeO₂-CaO possessed a < 5% decrease for CO and C1 yield (CO₂ + CO + CH₄) and > 99% CO selectivity after 20 cycles, indicating



Fig. 8. Real-time performance of various Ni/support-CaO BCMs over ICCU-RWGS at 650 °C: (a) CO₂ capture performance collected on TGA; (b) CO₂ conversion and CO selectivity; (c) CO generation rate and CO₂ conversion (d) under various temperature over Ni/CeO₂-CaO.



Fig. 9. Cycle performance of Ni/CeO₂-CaO over ICCU-RWGS at 650 °C.

the excellent and stable ICCU-RWGS performance. Notably, the overall CO_2 conversion slightly increased from 56.07% in the 1st cycle to 62.03% in the 20th cycle, which outperforms the state-of-art ICCU-RWGS performance using similar conditions (Table 2). It is believed that the effective reactant spillover onto catalytic sites is critical in the catalytic process [51]. As shown in Fig. 6e, Ni/CeO₂ and CaO exhibited closer contact in spent Ni/CeO₂-CaO, indicating a shorter CO₂ spillover distance. The self-optimisation of Ni/CeO₂-CaO bifunctional combined material in ICCU-RWGS might be attributed to the volume expansion–shrinkage effect of the sol–gel CaO in cyclic carbonation-hydrogenation, which partially embedded Ni/CeO₂ onto the surface

layer of CaO.

4. Conclusions

In this work, several Ni/support-CaO bifunctional combined materials (BCMs) were prepared by physically mixing sol-gel CaO and Ni catalysts with various supports (ZrO₂, TiO₂, CeO₂ and Al₂O₃). The CO₂ adsorption and catalytic performance of Ni/support-CaO BCMs were evaluated via integrated CO2 capture and reverse water-gas shift (ICCU-RWGS) process at different temperatures from 550 to 750 °C. The Ni/ CeO_2 -CaO outperformed the other Ni/support-CaO (support = ZrO_2 , TiO₂ or Al₂O₃) over ICCU-RWGS performance (CO₂ adsorption and catalytic activity). The enhanced CO₂ adsorption performance was attributed to the stronger basicity of Ni/Al₂O₃ and Ni/CeO₂. And the improved catalytic performance (CO2 conversion, CO yield and CO generate rate) was related to the excellent Ni dispersion and reducibility. The spinel formation contributed to the Ni species dispersion by forming strong interaction with support; however, only the easy-reducible spinel (NiTiO₃) was active in the ICCU process. Furthermore, the Ni/CeO₂-CaO exhibited excellent stability in 20 cycles of ICCU and showed a selfoptimising trend in CO₂ conversion (56.07% and 62.03% for the 1st and 20th cycles, respectively) due to the gradually close distance between CaO and Ni/CeO₂ owing to the volume expansion and shrinkage of CaO during carbonation-hydrogenation cycles.

CRediT authorship contribution statement

Shuzhuang Sun: Conceptualization, Methodology, Formal analysis,

Table 2

Comparison of ICCU-RWGS performance of Ni/CeO₂-CaO and materials from literature.

Materials	Mixture method	ICCU condition	CO ₂ capacity	CO_2 conv.	CO sel.	Cycle stability	Ref.
Ni/CeO2-CaO (~3.3% Ni)	Physical mixture	Adsorption: 650 °C, 20% CO ₂ /N ₂	9.6	62%	100%	20	This work
		Hydrogenation: 650 °C, 5% H ₂ /N ₂					
Ni/CeCaCO3	impregnation	Adsorption: 550 °C, 20% CO ₂ /N ₂	10.0	42%	26%	n.a.	[32]
		Hydrogenation: 550 °C, 5% H ₂ /N ₂					
1 %NiCaO	One-pot	Same as above	9.2	38%	42%	n.a.	[32]
10 %NiCaO	One-pot	Same as above	8.1	45%	31%	n.a.	[32]
Ni/CS	wet-mixing	Adsorption: 650 °C, 10% CO ₂ /N ₂	3.6	21.9%	n.a.	5	[25]
		Hydrogenation: 650 °C, 5% H ₂ /N ₂					
Ni/CS-P30	Impregnation	Same as above	8.4	34%	n.a.	5	[25]
Ni/CS-P30-C	Impregnation	Same as above	13.3	39%	n.a.	5	[25]
Ca ₁ Ni _{0.1}	One-pot	Adsorption: 650 °C, 15% CO ₂ /N ₂	15.0	46%	n.a.	20	[20]
		Hydrogenation: 650 °C, 5% H ₂ /N ₂					
Ca1Ni0.1Ce0.017	One-pot	Same as above	14.2	51%	n.a.	n.a.	[20]
Ca1Ni0.1Ce0.033	One-pot	Same as above	14.1	52%	n.a.	20	[20]

Investigation, Data curation, Writing – original draft. Chen Zhang: Methodology, Investigation, Formal analysis. Shaoliang Guan: Formal analysis, Investigation, Resources. Shaojun Xu: Formal analysis, Resources, Writing – review & editing, Supervision. Paul T. Williams: Formal analysis, Resources, Writing – review & editing, Supervision. Chunfei Wu: Conceptualization, Writing – review & editing, Supervision, Project administration, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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. The UK Catalysis Hub is kindly thanked for the resources and support provided via our membership of the UK Catalysis Hub Consortium and funded by EPSRC grant: EP/R026939/1, EP/R026815/1, EP/R026645/1, EP/R027129/1 or EP/M013219/1(biocatalysis). The XPS data collection was performed at the EPSRC National Facility for XPS ('HarwellXPS'), operated by Cardiff University and UCL, under contract No. PR16195.

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