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The Effect of Alkali Metals (Li, Na, and K) on Ni/CaO Dual-Functional Materials for Integrated CO₂ Capture and Hydrogenation

Yong Hu, Qian Xu ^{*} , Yao Sheng , Xueguang Wang ^{*}, Hongwei Cheng , Xingli Zou and Xionggang Lu 

State Key Laboratory of Advanced Special Steel, School of Materials Science and Engineering, Shanghai University, 99 Shangda Road, BaoShan District, Shanghai 200444, China; huyongsh@163.com (Y.H.); shengyao@shu.edu.cn (Y.S.); hwcheng@shu.edu.cn (H.C.); xlzou@shu.edu.cn (X.Z.); luxg@shu.edu.cn (X.L.)

^{*} Correspondence: qianxu@shu.edu.cn (Q.X.); wxg228@shu.edu.cn (X.W.)

Abstract: Ni/CaO, a low-cost dual-functional material (DFM), has been widely studied for integrated CO₂ capture and hydrogenation. The core of this dual-functional material should possess both good CO₂ capture–conversion performance and structural stability. Here, we synthesized Ni/CaO DFMs modified with alkali metals (Na, K, and Li) through a combination of precipitation and combustion methods. It was found that Na-modified Ni/CaO (Na-Ni/CaO) DFM offered stable CO₂ capture–conversion activity over 20 cycles, with a high CO₂ capture capacity of 10.8 mmol/g and a high CO₂ conversion rate of 60.5% at the same temperature of 650 °C. The enhanced CO₂ capture capacity was attributed to the improved surface basicity of Na-Ni/CaO. In addition, the incorporation of Na into DFMs had a favorable effect on the formation of double salts, which shorten the CO₂ capture and release process and promoted DFM stability by hindering their aggregation and the sintering of DFMs.

Keywords: alkali metal; Ni/CaO; dual-functional material; CO₂ capture and hydrogenation; reverse water–gas shift



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1. Introduction

The excessive emissions of anthropogenic CO₂ into the atmosphere are recognized as a primary driver of global warming and climate change [1–3]. To combat this issue, collaborative efforts from researchers and governments are required to curtail CO₂ emissions. Carbon capture and storage (CCS) have been considered the primary strategy to achieve emission reduction targets, but its high cost and significant energy consumption in CO₂ purification, compression, and transportation limit its widespread application [4–7]. An alternative approach, known as CO₂ capture and utilization (CCU), aims to convert the captured CO₂ into value-added fuels and chemicals, offering a promising solution to the CO₂ challenge [8–10]. Integrated CO₂ capture and utilization (ICCU) technology, which combines capture and conversion in a single column under the same temperature, has garnered increasing interest due to its potential to reduce capital and operating costs while saving energy [11–13].

Generally, the successful implementation of ICCU relies on the development of dual-functional materials (DFMs) capable of serving as both CO₂ adsorbents and catalytic components for CO₂ conversion. DFMs cyclically capture CO₂ from combustion flue gas with a CO₂ concentration of 4–14 vol%, subsequently converting the adsorbed CO₂ into valuable products, such as synthetic fuels or other chemicals, while regenerating the adsorbent. CO₂ adsorbents are typically based on alkaline or alkaline–earth compounds, as they react with acidic CO₂ to form corresponding carbonates. Among these materials, CaO-based composites are extensively studied in ICCU processes, due to their low cost, high availability (e.g., limestone), and excellent theoretical CO₂ capacity (17.8 mmol/gCaO) [14,15]. On

the other hand, catalysts such as Pt [16], Ni [17], or Fe [18] are widely used to catalyze the C1 chemistry reactions, including methanation, reverse water–gas shift (RWGS), and dry reforming of methane (DRM) in ICCU processes for CO₂ conversion. As a result, Ni/CaO DFMs are extensively employed in ICCU technology due to their optimal cost-to-activity ratio [19–27]. However, the development of Ni/CaO DFMs with both high CO₂ capture capacity and efficient catalytic activity remains a significant challenge since most CO₂ conversion reactions are conducted outside at a high temperature, but CaO does not maintain its stability during carbonation–calcination cycles at high temperatures, given the relatively low Tammann temperature of CaCO₃ (533 °C). Numerous efforts have been dedicated to resolving this sintering issue. In previous studies, we successfully applied a three-dimensional Ni/CaO network composed of mesopores and macropores in a stable high-temperature ICCU process thanks to its unique porosity structure [28,29]. Recently, the doping approach of DFMs with alkali metals, such as Li, Na, K, and Cs, has been considered a promising strategy to promote the ICCU process. Previous research has developed Ca adsorbents and investigated the promoting effect of alkali metals. Ahmed et al. conducted a study on a series of double salts, which included K- and Na-promoted Ca adsorbents, specifically designed for CO₂ capture at 650 °C. The results of their research showed that the K–Ca double salt displayed an exceptional CO₂ adsorption capacity of 10.7 mmol/g [30]. The K–Ca double-salt materials were also utilized in a combined CO₂ capture–utilization process aimed at producing syngas [31]. In this process, the CO₂ sorption capacity was measured at 0.95 mmol/g, with a CO₂ conversion rate of 65%. However, there are limited studies available on the subject of integrated CO₂ capture and hydrogenation utilizing alkali-metal-doped Ni/CaO catalysts.

Herein, we successfully synthesized and utilized modified Ni/CaO dual-functional materials for integrated CO₂ capture (Equation (1)) and reverse water–gas shift (RWGS) reaction (Equation (2)). The RWGS reaction is a highly valuable CO₂ conversion process that provides a promising opportunity to align the high temperature required for CO₂ capture with the generation of CO, which can be further utilized as a raw material in various chemical processes to produce valuable chemicals [32]. To achieve this, we employed a facile precipitation–combustion method to synthesize Ni nanoparticles modified with alkali metals (Na, K, and Li) on CaO (M-Ni/CaO), creating effective DFMs for selective CO production through ICCU. Thorough investigations of the physical and chemical properties of the modified Ni/CaO DFMs were conducted using techniques such as XRD, N₂ adsorption–desorption, SEM, EDX, TEM, CO₂-TPD, and TG. The introduction of different doping elements (Na, K, and Li) into the Ni/CaO DFMs had a profound impact on CO₂ capture and CO formation. Additionally, we assessed the cycle stability of the Na-doped Ni/CaO DFMs by performing 20 cycles of integrated CO₂ capture and hydrogenation. The evaluation results are promising and are expected to provide valuable guidance for the development of highly effective DFMs and the establishment of an efficient pathway to enhance ICCU technology.



2. Experimental Section

2.1. Preparation of Ni/CaO and M/CaO (M = Li, Na, and K) DFMs

All reagents were procured from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) and utilized without any additional purification steps. All gases were procured from Shanghai Youjiali Liquid Helium Co., Ltd. (Shanghai, China) and had a nominal purity of at least 99.99%. For Li-doped Ni/CaO DFM, 0.70 g of nickel nitrate hexahydrate (Ni(NO₃)₂·6H₂O), 22.14 g of calcium nitrate tetrahydrate (Ca(NO₃)₂·4H₂O), 0.28 g of lithium carbonate (Li₂CO₃), and 21.01 g of citric acid monohydrate (C₆H₈O₇·H₂O) were dissolved in 50 mL of an aqueous solution with a magnetic stirrer at 40 °C under sufficient

agitation. Then, 1.0 mol/L of an ammonium carbonate ($(\text{NH}_4)_2\text{CO}_3$) solution was added dropwise using a peristaltic pump until the pH value of the mixed solution reached 8.0, where the nickel and calcium were precipitated in the form of carbonates species. The suspension was further evaporated in the superfluous water at 80 °C. The obtained solid was dried at 100 °C overnight and then calcined at 200 °C for 2 h and 700 °C for 5 h, with a heating rate of 2 °C/min. The precursor particles consisted of citric acid complexes and carbonated species of nickel and calcium, which underwent decomposition during the combustion stage at a high calcination temperature. The Na- and K-doped Ni/CaO DFM s were prepared using the same process as described above, and the mass fractions of Ni, the added carbonates, and CaO in each DFM were kept at 2.5 wt%, 5 wt%, and 92.5 wt%, respectively. The obtained sample was denoted as M-Ni/CaO, where M refers to the added alkali metal element (Li, Na, and K). For comparison, the Ni/CaO DFM was also prepared and used as the reference sample.

2.2. Characterization of Ni/CaO and M-Ni/CaO (M = Li, Na, and K) DFM s

The crystalline structures of the DFM s were investigated using a Bruker D8 Advance diffractometer to perform X-ray diffraction (XRD) with Cu K α radiation ($\lambda = 0.15418$ nm). The patterns were collected in the 2θ range of 10° to 90° with a scanning speed of 8°/min. The actual masses of Ni and alkali metal elements (Li, Na, and K) in the DFM s were measured via inductively coupled plasma–atomic emission spectrometry (ICP–AES) conducted on a PerkinElmer emission spectrometer. The specific surface area and the pore size distribution were determined via N₂ adsorption–desorption at −196 °C on a Micromeritics ASAP 2020 Sorptometer (Micromeritics Instrument Ltd., Shanghai, China). The DFM s were degassed for 6 h at 200 °C prior to each measurement. The surface morphologies and elemental distribution of the DFM s were performed using an FEI Nova Nano SEM 450 (FEI Company, Hillsboro, OR, USA) scanning electron microscope (SEM) coupled with an EDAX energy-dispersive X-ray spectrometer. All samples were sputtered with a thin layer of Pt via low-vacuum sputter coating before imaging via SEM. The transmission electron microscope (TEM) images of the DFM s were obtained on a JEOL JEM-2010F field-emission scanning electron microscope operating at a working voltage of 200 kV. CO₂ temperature-programmed desorption (CO₂-TPD) of the DFM s was determined using an automatic PCA-1200 (Beijing builder Co., Ltd., Beijing, China) chemisorption analyzer. Prior to each measurement, 0.2 g of DFM s was used for pretreatment with Ar at 700 °C for 1 h and then cooled to room temperature. Then, chemical adsorption was conducted using a 10 vol% CO₂/Ar for 1 h at 80 °C, followed by desorption under pure Ar at temperatures ranging from room temperature to 900 °C.

2.3. CO₂ Capture and Capture–Release of Ni/CaO and M-Ni/CaO (M = Li, Na, and K) DFM s

CO₂ capture and capture–release experiments of the DFM s were conducted using an SDT650 (TA Instruments, New Castle, DE, USA) thermogravimetric analyzer. For the CO₂ capture experiment, approximately 8 mg of each DFM was heated to a test temperature (550, 600, 650, or 700 °C) at a heating rate of 10 °C/min in pure Ar at 100 mL/min for 0.5 h to eliminate impurities. Subsequently, a 10 vol% CO₂/Ar at 100 mL/min was introduced for CO₂ capture for 2 h. For the CO₂ capture–release test, about 8 mg of each DFM was heated up to 650 °C in pure Ar for 0.5 h. After 0.5 h of CO₂ capture in 10 vol% CO₂/Ar at 100 mL/min, pure Ar was introduced for CO₂ release for 1.5 h. Additionally, 10 cycles of CO₂ capture–release tests were performed to evaluate the cyclic stability of the DFM s.

2.4. Integrated CO₂ Capture and Hydrogenation of Ni/CaO and M-Ni/CaO (M = Li, Na, and K) DFM s

The integrated CO₂ capture and hydrogenation were conducted in a fixed-bed column with a vertical quartz reactor. A thermocouple was put in the middle of the reactor to detect the actual bed temperature. The reactants CO₂ and H₂, as well as the dilution gases of Ar, were precisely controlled with mass flow controllers (MFCs) and thoroughly mixed before

being introduced into the reactor. Briefly, 1 g of the pelletized sample was pre-reduced in a 10 vol% H₂/Ar (100 mL/min) at 650 °C for 3 h. Then, CO₂ capture was conducted in a 10 vol% CO₂/Ar (100 mL/min) for 1 h. Subsequently, the DFMs were hydrogenated in a 10 vol% H₂/Ar (100 mL/min) after the reactor was purged with Ar for 10 min. The outlet gas was analyzed online using a GC9800 gas chromatograph. In addition, 20 cycles of combined CO₂ capture and hydrogenation were performed to investigate the cyclic stability of Na-Ni/CaO.

The concentrations of the reactants (CO₂ and H₂) and the product (CO) in the outlet gases were calculated based on Equation (3). In addition, there was no CH₄ detected in the outlet gases. The conversion of CO₂ (C_{CO₂}) was calculated by following Equation (4).

$$F_i (\%) = \frac{[i]}{[H_2] + [CO] + [CO_2]} \times 100\% \quad (3)$$

$$C_{CO_2} (\%) = \frac{F_{CO}}{F_{CO_2} + F_{CO}} \times 100\% \quad (4)$$

An SDT650 (TA Instruments, New Castle, DE, USA) thermogravimetric analyzer was used to analyze the capacities of the captured and released CO₂ of DFMs. The DFMs before and after the CO₂ capture stage or the hydrogenation stage were heated to 1000 °C in pure Ar. The CO₂ capture (N_{ac}), release capacity (N_{dc}), carbon balance, and CO yield (Y_{CO}) of DFMs were calculated based on the following equations:

$$N_{ac} (\text{mmol/g}) = \frac{(m_0 - m_1) \times 1000}{m_1 \times M_{CO_2}} \quad (5)$$

$$N_{dc} (\text{mmol/g}) = N_{ac} - \frac{(m_2 - m_3) \times 1000}{m_3 \times M_{CO_2}} \quad (6)$$

$$\text{Carbon balance} (\%) = \frac{N_{dc}}{N_{ac}} \times 100\% \quad (7)$$

$$Y_{CO} (\text{mmol/g}) = N_{dc} \times C_{CO_2} \quad (8)$$

where m_0 and m_1 represent the masses of the DFMs before and after the CO₂ capture stage, m_2 and m_3 represent the masses of the DFMs before and after the hydrogenation stage, and M_{CO_2} represents the molecular weight of CO₂.

3. Results and Discussion

3.1. Characterization of the Ni/CaO and M-Ni/CaO (M = Li, Na, and K) DFMs

Figure 1a includes the XRD patterns of the calcined Ni/CaO modified with alkali metals (Li-Ni/CaO, Na-Ni/CaO, and K-Ni/CaO) and Ni/CaO. Intense and narrow diffraction peaks at around 32.2°, 37.3°, 53.9°, 64.2°, and 67.4° could be observed for all the prepared materials, which are characteristic of highly crystalline CaO with a cubic structure [33]. The weak peaks around 18.1° and 34.1° are characteristic of Ca(OH)₂, which is related to the existence of moisture. Furthermore, small diffraction peaks at 43.3° and 62.8° are ascribed to the characteristic peak of NiO. The addition of Na and K did not give rise to new crystalline phases, indicating that alkali metals were present in an amorphous and/or highly dispersed state, and the crystalline structure of the CaO remained unchanged, but a slight decrease in the intensity of the characteristic diffraction peaks of NiO was observed for Na-Ni/CaO and K-Ni/CaO compared with Ni/CaO, which is attributed to the stabilization of metal particles caused by the doping of alkali metals [34,35]. However, a new peak with higher crystallinity attributed to Li_{0.3}Ni_{1.7}O₂ was detected for Li-Ni/CaO [36].

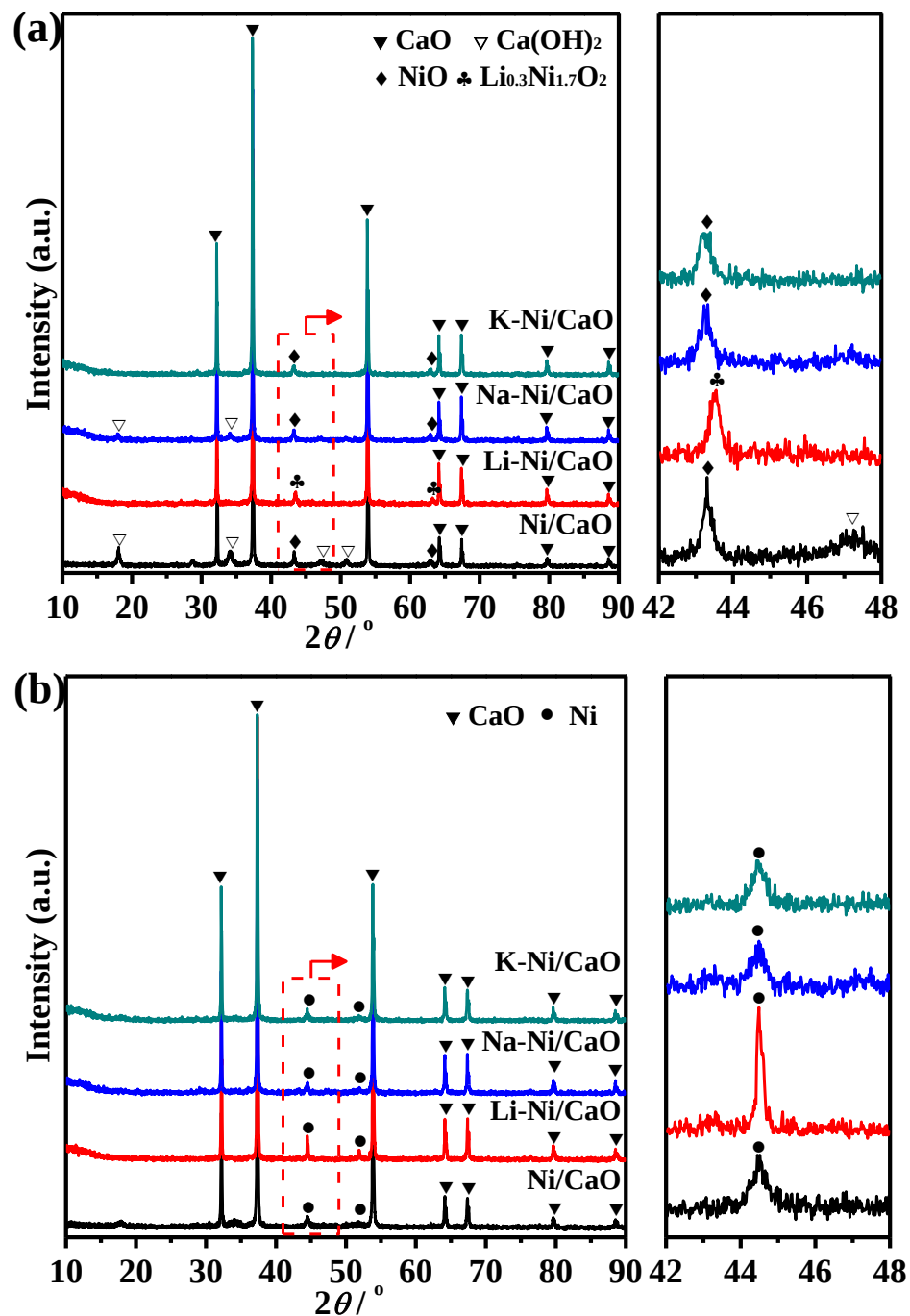


Figure 1. XRD patterns of (a) calcined and (b) reduced Ni/CaO and M-Ni/CaO (M = Li, Na, and K) DFM.

The crystal phase of the different samples after subjecting them to the reduction pretreatment at 650 °C in the 10 vol% H₂/Ar mixture for 3 h was also assessed in the XRD patterns (Figure 1b). All samples maintained the intense and narrow diffraction peaks belonging to CaO, indicating the high stability of this oxide. As expected, no characteristic diffraction peaks were discernible for Ca(OH)₂, Li_{0.3}Ni_{1.7}O₂, and NiO phases. Diffraction peaks at 44.5° and 51.8° were ascribed to metallic Ni, which originated from the reduction of NiO and/or Li_{0.3}Ni_{1.7}O₂. The average crystallite sizes of Ni in the reduced materials were estimated using the Scherrer equation, and the results are shown in Table 1. Na-Ni/CaO and K-Ni/CaO presented relatively smaller Ni crystallites, indicating that the addition of Na and K was conducive to the dispersion of Ni. The small size of Ni particles

is considered crucial for achieving high catalytic activity in CO₂ hydrogenation [37,38]. Therefore, as Li-Ni/CaO had larger Ni crystallites than Ni/CaO, it revealed the most severe Li_{0.3}Ni_{1.7}O₂ aggregation.

Table 1. Physicochemical properties of the reduced Ni/CaO and M-Ni/CaO (M = Li, Na, and K) DFMs.

Materials	Ni (wt%) ^a	Alkali Metal (wt%) ^a	S _{BET} (m ² /g)	V _p (cm ³ /g)	D _p (nm)	Ni Crystallite Size (nm) ^b	Ni Particle Size (nm) ^c
Ni/CaO	2.33	N.A.	16.3	0.11	23.7	16.0	15.0 ± 3.1
Li-Ni/CaO	2.31	1.03	5.9	0.04	19.8	22.9	21.8 ± 3.8
Na-Ni/CaO	2.37	2.12	12.6	0.10	23.1	12.9	12.2 ± 2.0
K-Ni/CaO	2.34	2.76	12.2	0.09	22.8	13.7	13.3 ± 2.3

^a Determined via ICP analysis. ^b Ni crystallite size was calculated using the Scherrer equation. ^c Ni particle size was measured using TEM.

Regarding textural properties, Figure 2 shows the N₂ adsorption–desorption isotherms and pore size distributions for the reduced DFMs. All of them exhibited a type-IV isotherm and an H3-shaped hysteresis loop, which are characteristic of slit-shaped pores formed by the decomposition of the citric acid complex and carbonated species. As shown in Table 1, the addition of alkali metals to Ni/CaO resulted in a slight decrease in the specific surface areas to 12.6 and 12.2 m²/g for Na-Ni/CaO and K-Ni/CaO, respectively, whereas these DFMs maintained comparable pore volumes as well as average pore sizes. As for Li-Ni/CaO, the specific surface area, pore volume, and average pore size dramatically decreased to 5.9 m²/g, 0.04 cm³/g, and 19.8 nm, respectively, due to the pore structure blockage caused by the large Li_{0.3}Ni_{1.7}O₂ particles. The larger specific surface area of DFMs is believed to correlate with high CO₂ capture capacity [39]. In addition, Figure 2 shows that Na-Ni/CaO and K-Ni/CaO maintained bimodal pore size distributions with mesopores in the range of 2–5 nm and macropores in the range of 20–100 nm, which was similar to the pore structure of three-dimensional networks consisting of meso- and macropores with excellent elasticity and stability for Ni/CaO, as previously reported [30,31]. Meso- and macropores are responsible for CO₂ uptake and diffusion control, respectively [40].

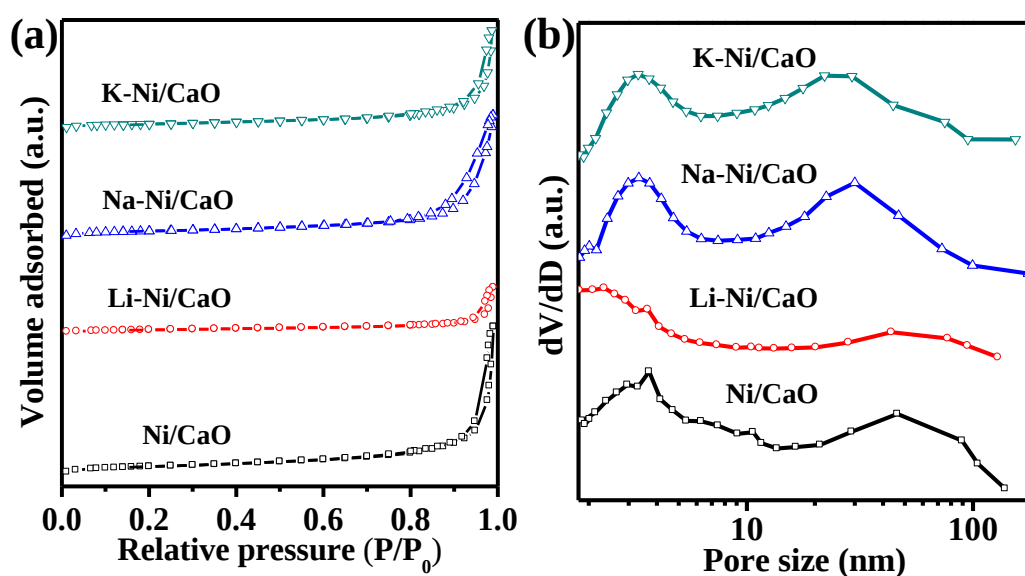


Figure 2. (a) N₂ adsorption–desorption isotherms and (b) pore size distributions of the reduced Ni/CaO (□), Li-Ni/CaO (⊙), Na-Ni/CaO (△) and K-Ni/CaO (▽) DFMs.

To investigate the effect of alkali metal doping on the morphology and particle size of the reduced DFMs, SEM/EDX and TEM were conducted. As shown in Figure 3a–d, the Ni/CaO DFMs prepared via a facile precipitation–combustion method exhibited a three-dimensional network with porous morphology, which was composed of CaO particles ranging in size from 50 to 100 nm. The porous morphology was maintained very well after doping with alkali metals, including Na and K. However, it was noticed that the porous structure of Li-Ni/CaO partly collapsed, which agreed with the obvious decrease in specific surface areas. Additionally, SEM-EDX analysis was conducted to explore the distribution mappings of Na, Ni, and Ca elements in Na-Ni/CaO (Figure 3e,f). As could be observed, Na (blue color), Ni (red color), and Ca (yellow color) elements coexisted with a homogeneous distribution in all the analyzed areas, indicating their good dispersion. From the TEM image of Ni/CaO (Figure 4a), some dark crystal particles were observed with a mean size of ca. 15 nm distributed on the surface, where the lattice distance of 0.203 nm could be clearly seen and represented the lattice plane (111) of the metallic Ni phase [41]. After doping with alkali metals, the average sizes of Ni nanoparticles on the Li-, Na-, and K-Ni/CaO DFMs varied as 21.8 ± 3.8 nm, 12.2 ± 2.0 nm, and 13.3 ± 2.3 nm (Figure 4b–d), respectively, which was consistent with the XRD results (Table 1), suggesting that the introduction of Na or K into Ni/CaO DFMs certainly help to uniform and stabilize Ni particles to achieve the expected catalytic activity.

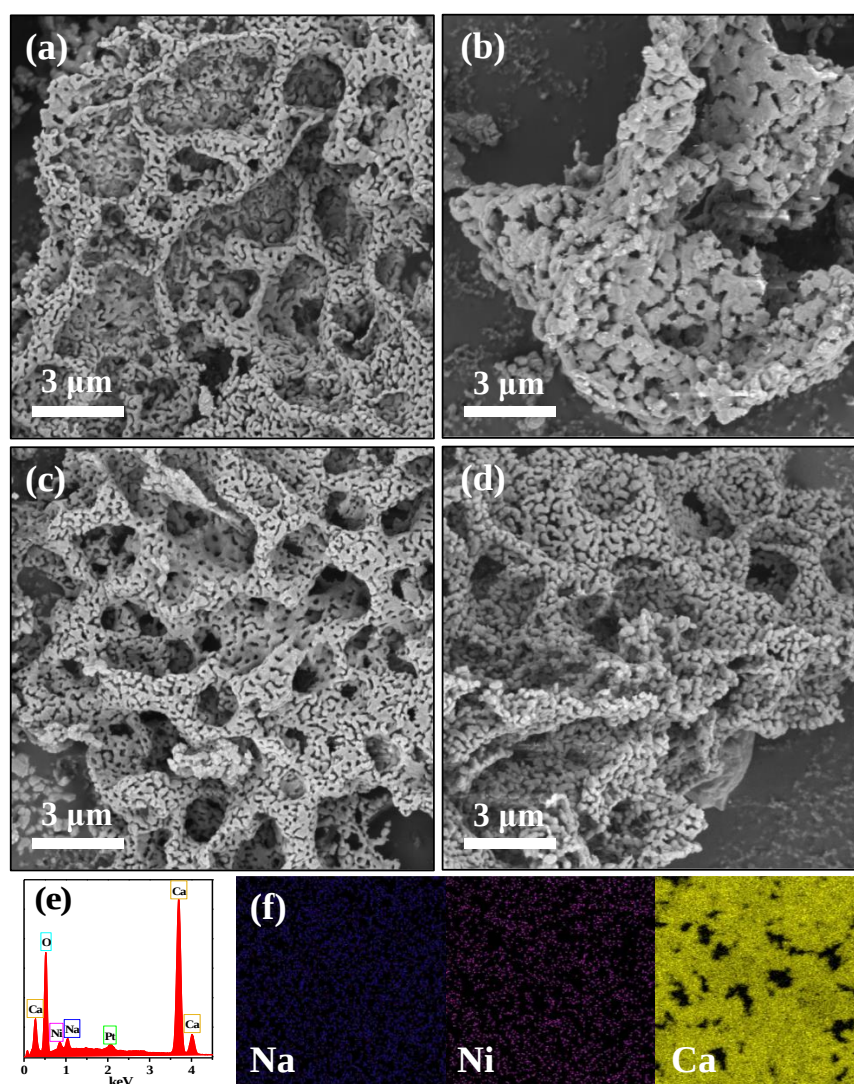


Figure 3. SEM images of (a) Ni/CaO, (b) Li-Ni/CaO, (c) Na-Ni/CaO, (d) K-Ni/CaO DFMs, and (e) EDX and (f) elemental mappings of Na-Ni/CaO DFM.

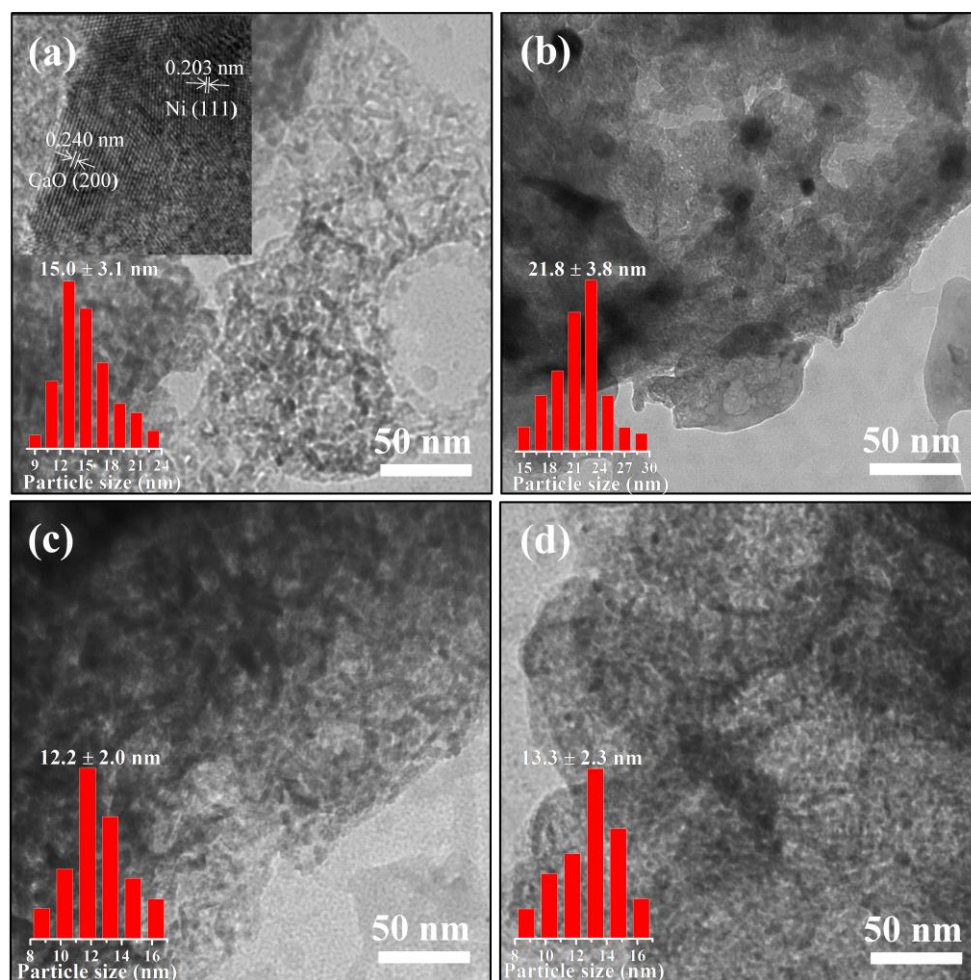


Figure 4. TEM images of (a) Ni/CaO, (b) Li-Ni/CaO, (c) Na-Ni/CaO, and (d) K-Ni/CaO DFMs.

The effect of alkali metal doping on CO₂ capture and activation was evaluated in CO₂-TPD experiments on Ni/CaO and M-Ni/CaO DFMs, which were pre-reduced in situ under H₂ at 650 °C before CO₂ adsorption at 80 °C. As shown in Figure 5, three types of CO₂ desorption peaks were detected for Ni/CaO: (1) the minor peak below 200 °C represents the desorption of the physisorbed CO₂ (classified as weak basic sites); (2) the peaks located in the temperature range of 250–550 °C typically originate from the chemisorbed CO₂ on the outer surface, including the Ca(OH)₂ phase (classified as medium basic sites); (3) the peaks located at temperature between 550 °C and 800 °C are attributed to CO₂ adsorbed at the bulk part of CaO particles (classified as strong basic sites) [19,42]. In comparison to Ni/CaO, the TPD profiles of Na-Ni/CaO and K-Ni/CaO exhibited similar types of basic sites but with a higher desorption temperature and an increase in peak intensity. As for the Li-Ni/CaO DFM, the low intensity of the desorption peaks suggested a relatively low CO₂ capture capacity. More specific information about the different basic site distributions was obtained from the integration of the corresponding desorption peaks. As presented in Table S1, the total basicity of the DFMs follows a descending order of Na-Ni/CaO (987.1 μmol/g) > K-Ni/CaO (879.5 μmol/g) > Ni/CaO (766.7 μmol/g) > Li-Ni/CaO (572.7 μmol/g). Particularly, the number of medium and strong basic sites, which were the main adsorption sites for CO₂, were significantly increased with Na or K doping, indicating that the deposition of Na or K onto CaO enhanced its affinity for CO₂ and endowed it with excellent CO₂ capture capability.

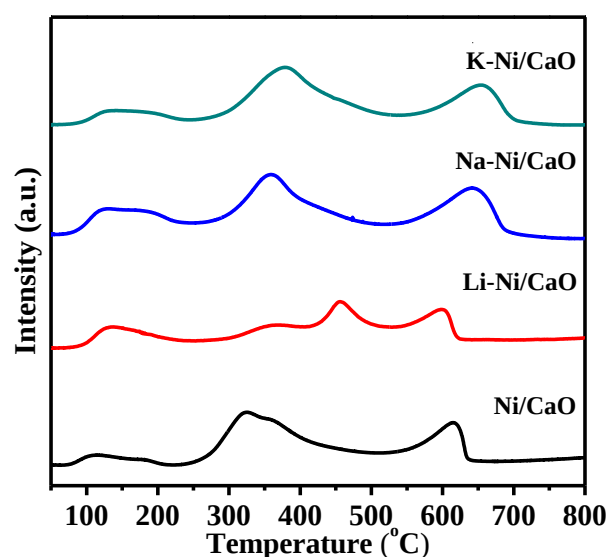


Figure 5. CO₂-TPD profiles of the reduced Ni/CaO and M-Ni/CaO (M = Li, Na, and K) DFMs.

3.2. CO₂ Capture and Capture–Release of Ni/CaO and M-Ni/CaO (M = Li, Na, and K) DFMs

The temperature of CO₂ capture in the DFMs was tested using the TGA technique under a simulated gas of 10 vol% CO₂/Ar over a wide temperature range of 50 °C to 1000 °C (Figure 6a). It could be observed that the weight of the as-prepared DFMs remarkably increased in the temperature range of 550–700 °C, in which CO₂ chemisorption could be activated to allow diffusion processes throughout the bulk of the materials. The carbonated CaO and alkali-metal-modified CaO were completely regenerated, with a sharp decrease in weight occurring at 740–800 °C, which corresponded to the decomposition of CaCO₃. This suggested that all DFMs exhibited good CO₂ capture capacities at temperatures between 550 °C and 700 °C. Furthermore, at 550, 600, 650, and 700 °C, the CO₂ isothermal capture capacities and adsorption rates of all DFMs increased with temperature and reached the maximum level at 650 °C (Figure S1 and Table S2).

Therefore, the isothermal CO₂ capture–release properties of all DFMs at 650 °C were investigated. As shown in Figure 6b, the capture of CO₂ on the DFMs followed two different processes. The CO₂ capture capacity exhibited a rapid increase during the initial stage (within 10 min), which was the chemical-reaction-controlled stage. Subsequently, it slowly increased in the latter stage (within 10–30 min), which was the product-layer-diffusion-controlled stage. Compared with Ni/CaO, the Na- or K-modified DFMs showed a higher CO₂ capacity both in the reaction-controlled and diffusion-controlled processes, contributing to a higher overall CO₂ capture capacity. The CO₂ capture capacities were ranked in the following order: Na-Ni/CaO (11.4 mmol/g) > K-Ni/CaO (10.3 mmol/g) > Ni/CaO (9.9 mmol/g) > Li-Ni/CaO (6.0 mmol/g). In addition, the alkali-metal-modified DFMs showed a shorter time span of CO₂ release than Ni/CaO, indicating the fast regeneration of the sorbents, which was essential to maintain its structural stability and mitigated CaO sintering [43,44]. The significantly enhanced desorption kinetics of a double-salt adsorbent containing K- and Na-CaO compared with that of bare CaO has previously been reported in several papers [30]. The XRD pattern of Na-Ni/CaO with 15 wt% Na doping after the capture of CO₂ showed the characteristic peaks of the Na₂Ca(CO₃)₂ phase (Figure S2), which confirmed the formation of double carbonates. The cycle stability of all DFMs was evaluated with 10 cycles of CO₂ capture and release at 650 °C (Figure 6c). Among them, Na-Ni/CaO showed the best cycle stability, retaining over 90% capacity after 10 cycles with only a slight decrease from 11.4 to 10.3 mmol/g, which was better than Ni/CaO (from 9.9 to 8.4 mmol/g). All these confirmed that not only CO₂ capture capacities but also the cycle stability of the modified DFMs were improved through the doping of Na and K.

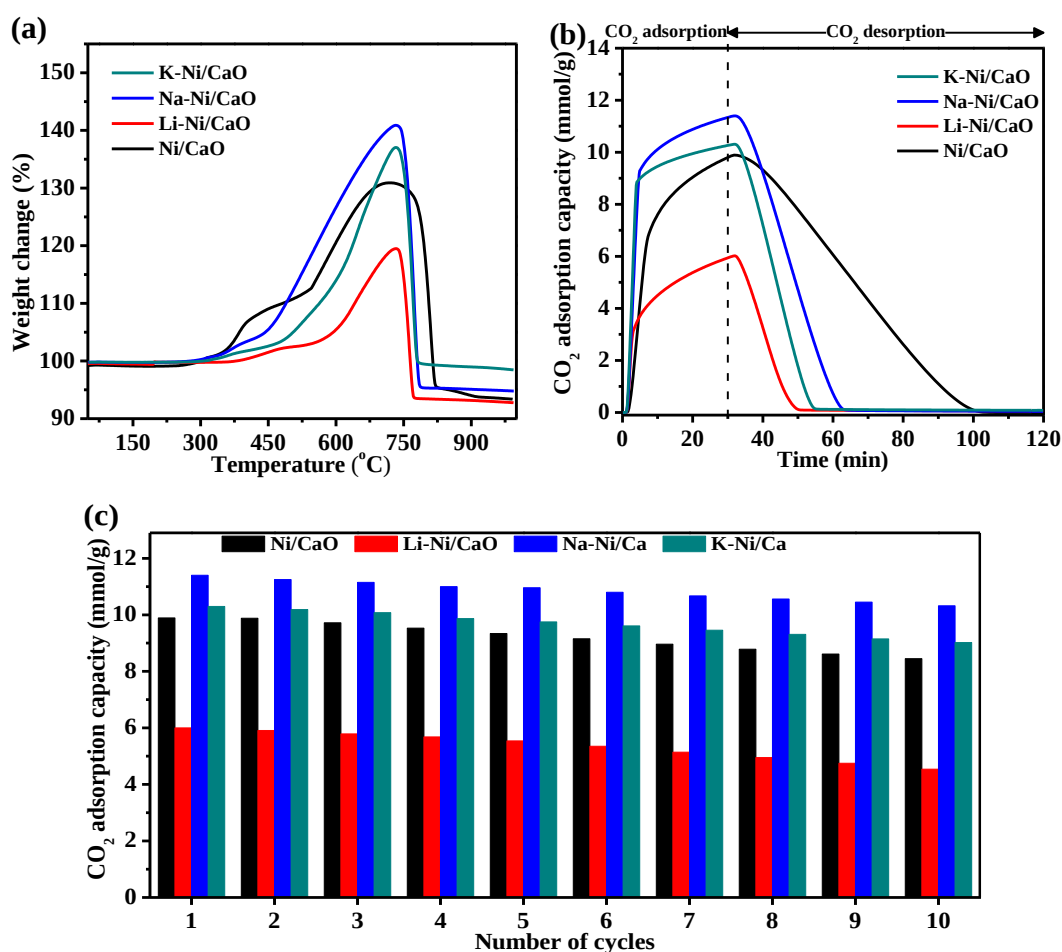


Figure 6. (a) The changes in the weights of Ni/CaO and M-Ni/CaO (M = Li, Na, and K) DFMs over the temperature range of 50 °C to 1000 °C; CO₂ capture–release profiles (b) and cyclic CO₂ capture–release stability (c) of Ni/CaO and M-Ni/CaO (M = Li, Na, and K) DFMs at 650 °C.

3.3. Integrated CO₂ Capture and Hydrogenation of Ni/CaO and M-Ni/CaO (M = Li, Na, and K) DFMs

The integrated CO₂ capture and hydrogenation performance of all the DFMs obtained from the fixed bed are illustrated in Figure 7. The whole process includes a CO₂ capture stage and a hydrogenation stage. In the CO₂ capture stage, a 10 vol% CO₂/Ar was introduced into the bed and was maintained for 1 h until the DFMs reached adsorption saturation. Based on the TG profiles of the DFMs after the CO₂ capture stage (Figure S3), the CO₂ capture capacities of all DFMs followed an ascending order: Li-Ni/CaO (7.0 mmol/g) < Ni/CaO (11.1 mmol/g) < K-Ni/CaO (11.6 mmol/g) < Na-Ni/CaO (12.0 mmol/g). This trend was consistent with the capture capacities illustrated in Figure S1 and the ranking of the number of medium and strong basic sites presented in Table S1. Following the CO₂ capture stage, pure Ar was introduced for 10 min to remove the excess CO₂ in the bed, and then it was switched to 10 vol% H₂/Ar to initiate the hydrogenation stage. As shown in Table 2, the Ni/CaO DFM achieved a CO₂ conversion rate and a CO yield of 60.3% and 6.3 mmol/g, respectively, with the hydrogenation stage lasting for 75 min until the complete decomposition of CaCO₃. It was found that the incorporation of secondary dopants into the NiO–CaO catalysts exerted a significant influence on the overall composition of the product gas, particularly with regard to the water–gas shift reaction [45]. The incorporation of Na and K in the Ni/CaO DFM resulted in higher CO₂ conversions and CO yields for the doped DFMs compared with Ni/CaO, indicating that the addition of Na and K could promote the hydrogenation of the calcium carbonate species (CaCO₃ and released CO₂) towards the production of CO by RWGS. In comparison, the hydrogenation stages of the

Na- and K-modified Ni/CaO DFMs were completed in only 45 min, owing to their high CO₂ conversion and rapid CO₂ release rates. Among all the DFMs, the Na-Ni/CaO DFM demonstrated the highest CO₂ conversion rate and CO yield of 62.0% and 7.1 mmol/g, respectively, which is attributed to its abundant basic sites and uniform dispersion of fine Ni particles. The preparation method, reaction types, testing conditions, CO₂ capture capacities, and product yields in the integrated CO₂ capture and hydrogenation using different Ni/CaO-based DFMs are listed in Table S3. The results demonstrated that the Na/Ni–CaO in this work exhibited significantly higher CO₂ capture capacity and better product yield than most Ni/CaO-based DFMs. Due to the larger Ni particle size and fewer basic sites caused by the poor pore structure, Li-Ni/CaO exhibited the lowest CO₂ capture capacity (7.0 mmol/g), CO₂ conversion rate (35.8%), and CO yield (2.3 mol/g) among all the DFMs. However, Li-Ni/CaO also underwent fast hydrogenation, i.e., within 55 min, possibly due to its low CO₂ capture capacity.

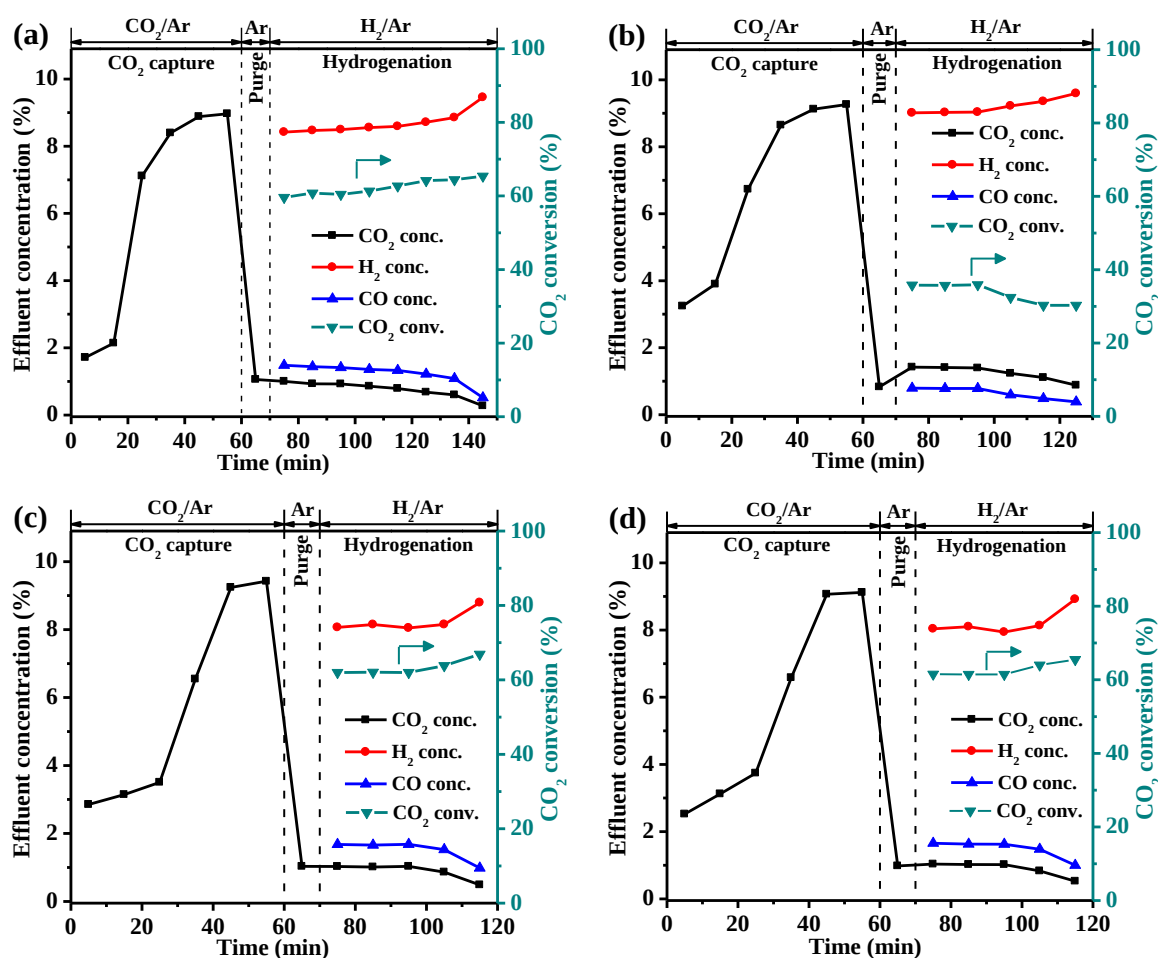


Figure 7. Integrated CO₂ capture and hydrogenation of (a) Ni/CaO ^a, (b) Li-Ni/CaO, (c) Na-Ni/CaO, and (d) K-Ni/CaO DFM. Temperature: 650 °C; GHSV: 6000 mL·g⁻¹·h⁻¹. ^a Reprinted with permission from ref [28]. Copyright 2023 Elsevier.

The carbon balance of the DFM was defined as the ratio between the total yields of CO₂ and CO in the hydrogenation stage and the CO₂ capture capacity in the capture stage. It was calculated that the carbon balances of all the DFMs were calculated to be higher than 90%, indicating that nearly all of the captured CO₂ in the capture stage was subsequently released as CO and CO₂ during the hydrogenation stage.

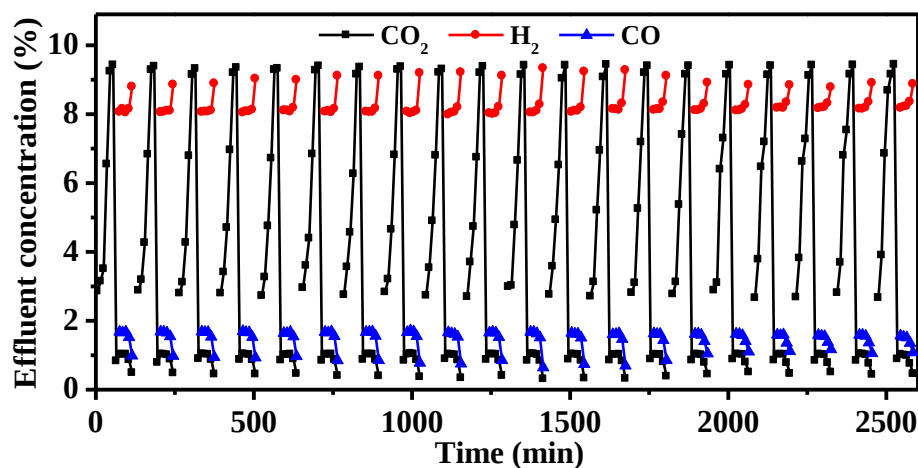
Table 2. The integrated CO₂ capture and hydrogenation performance of Ni/CaO and M-Ni/CaO (M = Li, Na, and K) DFM at 650 °C.

Materials	CO ₂ Capture (mmol/g) ^a	CO ₂ Conversion (%)	CO ₂ Yield (mmol/g)	CO Yield (mmol/g)	Carbon Balance (%) ^b
Ni/CaO ^c	11.1	60.3	4.2	6.3	94.4
Li-Ni/CaO	7.0	35.8	4.0	2.3	90.4
Na-Ni/CaO	12.0	62.0	4.4	7.1	95.8
K-Ni/CaO	11.6	61.5	4.2	6.8	95.4

^a CO₂ capture capacities were calculated with Equation (5) and are shown in Figure S3a. ^b Carbon balances were calculated with Equations (5)–(7) and are shown in Figure S3a,b. ^c Reprinted with permission from ref [28]. Copyright 2023 Elsevier.

3.4. The Cyclic Integrated CO₂ Capture and Hydrogenation of Na-Ni/CaO DFM

The cycle stability of the Na-Ni/CaO DFM was evaluated during 20 cycles of integrated CO₂ capture and hydrogenation. The change in CO₂, H₂, and CO concentrations over time are depicted in Figure 8. The Na-Ni/CaO DFM exhibited similar trends in the concentrations of CO₂, H₂, and CO with increasing cycle time, indicating a relatively stable conversion rate of CO₂. The spent Na-Ni/CaO achieved a CO₂ conversion rate of 60.5% after 20 cycles. As shown in Figure S4, it was determined that the spent Na-Ni/CaO retained a high CO₂ capture capacity of 10.8 mmol/g, indicating a mere 10% loss in capture capacity as compared to its initial performance. Figure 9 presents the SEM and TEM images of the spent Na-Ni/CaO after 20 cycles of the integrated process. The images show a slight aggregation of CaO particles and the disappearance of some mesopores, while the three-dimensional network's porous structure and macropores still remained stable (Figure 9a). Additionally, the porous structure of the spent Na-Ni/CaO was also analyzed using the N₂ adsorption–desorption isotherms and pore size distribution (Figure S5), which exhibited a slightly lower specific surface area and pore volume than those of fresh Na-Ni/CaO. In addition, the TEM image shows that the spent Na-Ni/CaO also maintained a uniform dispersion of Ni particles, with an average size of 14.5 nm after 20 cycles (Figure 9b). Furthermore, it is noteworthy that neither SEM nor TEM images reveal the existence of carbon deposition, indicating that the decline in CO₂ conversion could not be attributed to this factor. Therefore, we concluded that the great cycle stability of Na-Ni/CaO might be ascribed to the variation in Na species (Figure S2). One explanation is that Na₂O forms Na₂Ca(CO₃)₂, which is conducive to CO₂ capture and release and greatly shortens the cycle time of the whole integrated process. Another possibility is that Na₂Ca(CO₃)₂ can be reduced to Na₂O, which acts as a high-temperature refractory oxide to retard the sintering of CaO particles during the hydrogenation stage.

**Figure 8.** Twenty cycles of integrated CO₂ capture and hydrogenation of the Na-Ni/CaO DFM. Temperature: 650 °C; GHSV: 6000 mL·g^{−1}·h^{−1}.

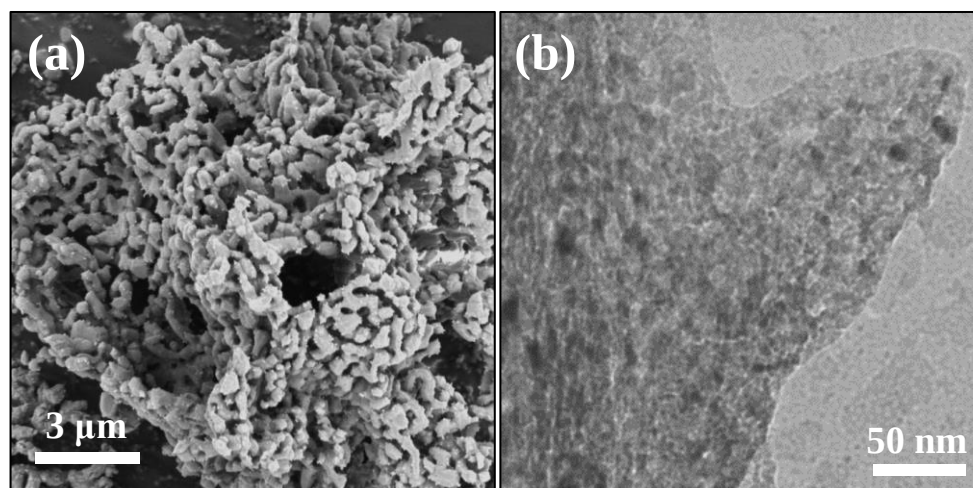


Figure 9. (a) SEM and (b) TEM images of the spent Na-Ni/CaO DFM after 20 cycles of integrated CO₂ capture and hydrogenation.

4. Conclusions

In this study, we successfully synthesized and utilized Ni/CaO DFMs modified with alkaline metals (Li, Na, and K) for producing CO through integrated CO₂ capture and hydrogenation. The incorporation of Na and K into the DFMs significantly increased the surface basicity, resulting in an enhanced CO₂ capture capacity. Additionally, Na and K improved the dispersion of Ni particles, leading to smaller particle sizes in the modified DFMs, which in turn contributed to higher catalytic activity. The performance evaluation of the DFMs regarding CO₂ capture and release revealed that Na- and K-doped Ni/CaO DFMs demonstrated not only high CO₂ capture capacities but also faster kinetics for both capture and release, surpassing those of Ni/CaO alone. However, the negative effects of Li on the integrated CO₂ capture and hydrogenation were observed in the Li-Ni/CaO catalyst, which was due to the low surface basicity, pore structure blockage, and large Ni particle sizes. Among all the tested DFMs, Na-Ni/CaO exhibited the highest CO₂ capture capacity of 12.0 mmol/g and CO₂ conversion rate of 62.0% with a CO production yield of 7.1 mmol/g in the integrated CO₂ capture and hydrogenation process at 650 °C. Moreover, the formation of double salts, particularly Na₂Ca(CO₃)₂, played a crucial role in enhancing the CO₂ capture and release rate of the DFMs, contributing to their stability by preventing the aggregation and sintering of CaO. The recyclability and surface morphology of the spent material clearly indicated that Na-Ni/CaO had high stability even after undergoing 20 cycles.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/ma16155430/s1>, Table S1: Weak, medium, strong and total basicity of the reduced Ni/CaO and M-Ni/CaO (M = Li, Na, K) DFMs. Figure S1: CO₂ capture profiles in the temperature range of 550 to 700 °C for 2 h. (a) Ni/CaO, (b) Li-Ni/CaO, (c) Na-Ni/CaO, and (d) K-Ni/CaO; Table S2: The CO₂ capture capacities of the M-Ni/CaO (M = Li, Na, and K) DFMs at the temperature range of 550–700 °C for 2 h; Figure S2: XRD pattern of Na-Ni/CaO with 15% Na doping after (a) reduction, (b) CO₂ capture stage, and (c) integrated CO₂ capture and hydrogenation; Figure S3: TG profiles of all DFMs (a) after the CO₂ capture stage and (b) the hydrogenation stage; Figure S4: TG profile of the spent Na-Ni/CaO after adsorption in CO₂/Ar for 1 h; Figure S5: N₂ adsorption–desorption isotherms and pore size distribution (insert part) of Na-Ni/CaO DFM after 20 cycles of integrated CO₂ capture and hydrogenation. Table S3. The combined CO₂ capture and hydrogenation performance over our proposed Na-Ni/CaO DFM and recently documented Ni/CaO based DFMs.

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