

Self-Regenerative Ni-Doped $\text{CaTiO}_3/\text{CaO}$ for Integrated CO_2 Capture and Dry Reforming of Methane

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In this work, a new type of multifunctional materials (MFMs) called self-regenerative Ni-doped $\text{CaTiO}_3/\text{CaO}$ is introduced for the integrated CO_2 capture and dry reforming of methane (ICCDRM). These materials consist of a catalytically active Ni-doped CaTiO_3 and a CO_2 sorbent, CaO . The article proposes a concept where the Ni catalyst can be regenerated in situ, which is crucial for ICCDRM. Exsolved Ni nanoparticles are evenly distributed on the surface of CaTiO_3 under H_2 or CH_4 , and are re-dispersed back into the CaTiO_3 lattice under CO_2 . The Ni-doped $\text{CaTiO}_3/\text{CaO}$ MFMs show stable CO_2 capture capacity and syngas productivity for 30 cycles of ICCDRM. The presence of CaTiO_3 between CaO grains prevents CaO/CaCO_3 thermal sintering during carbonation and decarbonation. Moreover, the strong interaction of CaTiO_3 with exsolved Ni mitigates severe accumulation of coke deposition. This concept can be useful for developing MFMs with improved properties that can advance integrated carbon capture and conversion.

1. Introduction

Integrated CO_2 capture and utilization (ICCU) has been widely studied as a promising climate mitigation strategy for producing CO_2 -derived fuels or chemicals such as methane, synthetic gas (syngas, CO , and H_2), light olefins, and methanol.^[1] ICCU is a less energy-intensive process compared to conventional CO_2 capture and utilization (CCU). Conventional CCU involves separating CO_2 from waste streams through carbonation (capture) and decarbonation (regeneration), transporting it via pipelines, and converting it into value-added chemicals.^[2] ICCU uses dual functional materials (DFMs), catalysts combined with CO_2 sorbents, to directly convert captured CO_2 into fuels and chemicals without separating and transporting CO_2 .^[3] Ni/ CaO -based dual functional materials (DFMs) are commonly used in ICCU processes due to the excellent catalytic activity

of Ni and theoretical CO_2 capture capacity of CaO (17.8 mmol $\text{CO}_2/\text{g CaO}$) at temperatures ranging from 500 to 700 °C, which are relevant for CO_2 valorization.^[3,4] For example, Ni/ CaO -based DFMs have been applied to various ICCU schemes such as methanation,^[3,4c] reverse water gas shift (rWGS),^[4c,d] dry reforming of methane (DRM),^[4b,c,e,f] and oxidative dehydrogenation of ethane to ethylene.^[5] Among the reactions studied, the Integrated CO_2 capture and subsequent DRM (ICCDRM) process using Ni/ CaO -based DFMs is a promising strategy to convert two greenhouse gases, CO_2 and CH_4 , into useful industrial building blocks – syngas.^[4b,c,e,f]

The initial step for ICCDRM occurs when CO_2 is chemically absorbed from a waste stream by CaO to form CaCO_3 in the carbonation step, $\text{CaO}(\text{s}) + \text{CO}_2(\text{g}) \leftrightarrow$

$\text{CaCO}_3(\text{s})$. Then the desorbed CO_2 from CaCO_3 reacts with CH_4 to produce syngas via DRM over the adjacent Ni catalyst, $\text{CaCO}_3(\text{s}) + \text{CH}_4(\text{g}) \leftrightarrow \text{CaO}(\text{s}) + 2\text{CO}(\text{g}) + 2\text{H}_2(\text{g})$.^[4b,c] ICCDRM exhibits excellent decarbonation kinetics, $\text{CaCO}_3(\text{s}) \leftrightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$, by shifting the equilibrium toward the products (Le Chatelier's principle) because of continuous consumption of CO_2 by DRM; $\text{CO}_2(\text{g}) + \text{CH}_4(\text{g}) = 2\text{CO}(\text{g}) + 2\text{H}_2(\text{g})$.^[4e] However, ICCDRM does not have sufficient multicycle performance for industrial practicality due to a sharp decrease in syngas production after complete CO_2 desorption and coke deposition from CH_4 decomposition: $\text{CH}_4(\text{g}) \leftrightarrow \text{C}(\text{s}) + 2\text{H}_2(\text{g})$.^[4b]

Coke deposition is one of the primary deactivation mechanisms for Ni catalysts used for DRM and ICCDRM. The coke can be deposited easily over large Ni nanoparticles (>20 nm) with inherently weak interaction with the underlying support.^[6] Some of the deposited coke can be gasified via the reverse Boudouard reaction, $\text{C}(\text{s}) + \text{CO}_2(\text{g}) = 2\text{CO}(\text{g})$; however, the remaining coke can result in a gradual decrease in the CO_2 capture capacity and catalyst performance.^[4a-c,e] The coke deposition can form metal carbides that decompose into carbon and metal atoms or clusters.^[7] Continuous carbon accumulation can cause filamentous or whisker coke to separate active Ni metal nanoparticles from the support.^[7b] Filamentous coke is difficult to oxidize or remove because the interface between the metal nanoparticles and support is thermodynamically-stable.^[8] Therefore, enhancing the interaction between Ni and oxide supports/sorbents is essential to maintain catalytic performance and stability.

Another factor that diminishes the multicycle performance of Ni/ CaO -based materials for ICCDRM is the low thermal stability of CaO . The stress induced by the cyclical volume expansion and

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shrinkage from CaO to CaCO₃ (CaO: 16.9 cm³ g⁻¹ and CaCO₃: 36.9 cm³ g⁻¹) during carbonation and decarbonation^[9] can contribute to rapid pore collapse of the structure. Additionally, the lower Tammann temperature of CaCO₃ (533 °C) than the DRM operation temperature (≈700 °C) causes the loss of surface area and sintering-induced decrease in CO₂ capture capacity.^[9,10] During each cycle, the reversible phase transformation of CaO to CaCO₃ weakens the Ni-CaO metal support interaction, resulting in significant sintering of Ni nanoparticles.^[11]

The use of in-situ exsolved metal nanoparticles from a select family of reducible perovskite oxides (ABO₃) has been utilized to address issues such as coking and sintering in DRM reaction conditions.^[12] The perovskite oxide structure (ABO₃) consists of a large A-site cation (La, Nd, Ca, Sr, or Ba) and a smaller B-site cation (Ti, Fe, Co, or Ni) where catalytic metals are substituted.^[12f,13] There are many benefits to using exsolution to generate catalyst nanoparticles. For instance, the nanoparticles formed are homogeneously distributed throughout the support.^[14] The inherent strong interaction between the partially submerged (or socketed) exsolved metal nanoparticles and host perovskites can retard the thermal sintering of metal nanoparticles.^[15] The exsolved metal nanoparticles can undergo self-regeneration by re-incorporating into the host perovskite under oxidative conditions and then re-exsolving under reductive conditions. The self-regeneration mechanism can also suppress coke accumulation during redox experiments by in situ gasification to CO_x by surface lattice oxygen of the perovskite oxide.^[12b,16] The partially submerged or socked nanoparticles can also suppress filamentous coke growth between the metal nanoparticles and perovskite support.^[17]

The morphology of CaO plays an essential role in the CO₂ capture kinetics, CO₂ uptake capacity, and thermal stability.^[9,18] To improve the sinter-resistance behavior of CaO, inert metal oxide stabilizers with high Tammann temperatures, such as ZrO₂, SiO₂, Al₂O₃, CeO₂, or MgO, are introduced into the CaO structure. The CaO/CaCO₃ stabilization with oxide additives can improve CO₂ capture performance (kinetics and capacity) by enhancing CO₂ diffusion within the porous structure and preventing the densification of the CaO particles.^[9] In addition, inert oxide materials between CaO crystallite grains can minimize CaCO₃ volume expansion during the CO₂ capture step, alleviating the stress-induced sintering of CaO.^[9]

To make ICCDRM commercially viable, addressing issues such as enhancing CO₂ uptake capacity, sintering of CaO and Ni, and coke deposition is vital. This study discusses an exciting approach to improve ICCDRM multicycle stability by developing self-regenerative Ni/CaTiO₃/CaO multifunctional materials (MFMs). The Ni nanoparticles are exsolved from Ca(Ni_xTi_{1-x})O₃ perovskite oxide. The strong adherence of exsolved Ni nanoparticles to Ca(Ni_xTi_{1-x})O₃ perovskite decreases the Ni sintering rate and coke formation, allowing for long-term multicycle catalytic stability. The strong metal-support interaction between Ni and CaTiO₃ suppresses the growth of filamentous coke. Coke formed on the surface of Ni nanoparticles during the DRM step is gasified by CO₂ during carbonation. The Ni nanoparticles are also self-regenerated during the CO₂ capture step (oxidative conditions) and re-emerged during the subsequent DRM (reductive conditions). The presence of CaTiO₃ perovskite phase within CaO grains alleviates the thermal sintering of CaO/CaCO₃ phases.

The Ni/CaTiO₃/CaO MFMs were characterized for their CO₂ capture capacity and ICCDRM performance. The experiments were developed to elucidate the property function relation for Ni/CaTiO₃/CaO MFMs.

2. Results and Discussion

2.1. Structural, Morphological, and Textural Properties of Ni-Doped CaTiO₃/CaO MFMs

Figure 1a illustrates the schematic of Ni incorporation into the CaTiO₃ perovskite frameworks during calcination and in-situ Ni exsolution from Ca_{1+x}Ni_yTi_{1-y}O₃ perovskite during the ICCDRM process. For this study, Ca_{1+x}Ni_yTi_{1-y}O₃ perovskite materials with secondary phase of CaO were calcined at 800 °C to incorporate Ni into CaTiO₃ and avoid the formation of perovskite-like structures containing higher Ca/Ti ratios, such as Ca₃Ti₂O₇ and Ca₄Ti₃O₁₀, which form at higher temperatures above 1000 °C^[19] and are nonreducible materials. The emergence of Ni occurs under a reductive environment (i.e., H₂) at 800 °C. During the CO₂ capture step, the Ni nanoparticles are re-incorporated into the perovskite Ca_{1+x}Ni_yTi_{1-y}O₃ matrix and CaO capture CO₂ as a formation of CaCO₃. Then the Ni nanoparticles are exsolved (e.g., self-regeneration of Ni nanoparticles), CO₂ desorbed from CaCO₃ reacts with CH₄ to produce syngas (CO and H₂) during the DRM step.

The X-ray diffraction (XRD) patterns of Ca₁Ti₁, Ca₂Ti₁, Ca₂Ni_{0.02}Ti_{0.98}, and Ca₂Ni_{0.05}Ti_{0.95} were compared to investigate the crystalline structure of the synthesized MFMs (**Figure 1b,c**). For comparison, the XRD pattern of Ca₂Ni_{0.05} DFM was also measured (**Figure S1**, Supporting Information). As-prepared Ca₂Ni_{0.05} DFM showed sharp peaks of CaO (JCPDS No. 75–0264) and broad NiO (JCPDS No. 73–1519) without any CaNi alloy phases. After reduction at 800 °C, NiO was converted to Ni metal (JCPDS No. 45–1027). The Ca₂Ni_{0.02}Ti_{0.98} and Ca₂Ni_{0.05}Ti_{0.95} MFMs were synthesized with excess Ca to promote the formation of CaO/CaTiO₃ composite materials. The concentration of Ni was changed to determine the influence on the catalytic performance and regeneration capability. Empirically, when the tolerance factor (*t*) lies in the range of 0.8 – 1.0, the structure of perovskites is stable.^[20] Although the tolerance factor is a good predictor of the perovskite stability, the octahedron factor (*μ*), a constant used to predict lattice distortion, must lie in the range of 0.44 – 0.72 for B and O to form a stable BO₆ octahedron. The tolerance factor (*t*) and octahedron factor (*μ*) of CaTiO₃ are 0.97 and 0.45, respectively, indicating that a stable CaTiO₃ perovskite structure is expected. On the other hand, the tolerance factor (*t*) and the octahedron factor (*μ*) of CaNiO₃ are 1.01 and 0.39, respectively, meaning that NiO₆ octahedron would be unstable to form CaNiO₃ perovskite structures. The XRD patterns of Ca₁Ti₁ exhibited sharp peaks of orthorhombic CaTiO₃ perovskite phase (JCPDS No. 86–1393) without impurity. The prominent peaks located at 33.1, 47.5, and 59.4 2θ correspond to the (1 1 2), (2 2 0), and (2 0 4) lattice planes of the CaTiO₃ structure. The XRD patterns of Ca₁Ti₁, Ca₁Ni_{0.01}Ti_{0.99}, and Ca₁Ni_{0.02}Ti_{0.98} showed the sharp peaks of CaTiO₃ perovskite phase without a separate CaO phase (**Figure S2a**, Supporting Information). Although a small amount of Ni is added, the patterns of NiO peak was observed in MFMs with a Ca-to-(Ni+Ti) ratio

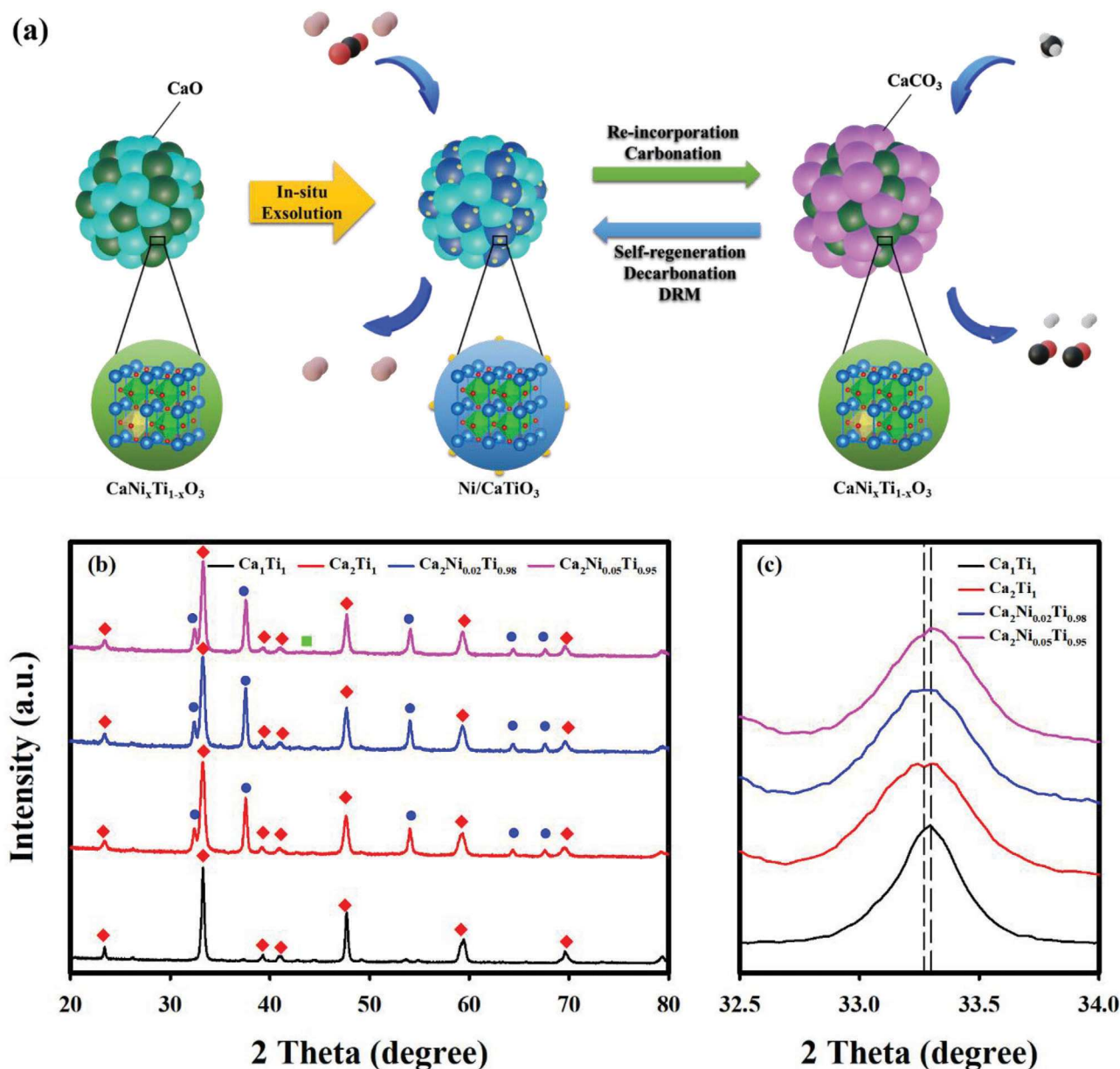


Figure 1. a) Schematic of in situ Ni nanoparticle exsolution from $\text{Ca}_{1+x}\text{Ni}_y\text{Ti}_{1-y}\text{O}_3$ perovskite and Ni re-incorporation into CaTiO_3 perovskite during ICCDRM process, b) XRD patterns and c) enlarged local XRD pattern of Ca_1Ti_1 , Ca_2Ti_1 , $\text{Ca}_2\text{Ni}_{0.02}\text{Ti}_{0.98}$ and $\text{Ca}_2\text{Ni}_{0.05}\text{Ti}_{0.95}$: $\blacklozenge$ CaTiO_3 , $\bullet$ NiO .

of 1, such as $\text{Ca}_1\text{Ni}_{0.01}\text{Ti}_{0.99}$ and $\text{Ca}_2\text{Ni}_{0.02}\text{Ti}_{0.98}$ (Figure S2b and Table S1, Supporting Information), which corresponds to the estimation from the predicted tolerance and octahedron factor for CaNiO_3 . For Ca_2Ti_1 , $\text{Ca}_2\text{Ni}_{0.02}\text{Ti}_{0.98}$, and $\text{Ca}_2\text{Ni}_{0.05}\text{Ti}_{0.95}$, it was observed that CaTiO_3 perovskite and CaO formed instead of the $\text{Ca}_3\text{Ti}_2\text{O}_7$ and $\text{Ca}_4\text{Ti}_3\text{O}_{10}$ phase. For $\text{Ca}_2\text{Ni}_{0.05}\text{Ti}_{0.95}$ MFM, a small NiO peak was observed. However, the peak of NiO was not observed in the $\text{Ca}_2\text{Ni}_{0.02}\text{Ti}_{0.98}$ MFM, showing a maximum solubility capacity for Ni dopants in the CaTiO_3 lattice (Figure S3a, Supporting Information). Estimated $\text{Ca}/(\text{Ni}+\text{Ti})$ ratio in perovskite obtained from STEM-EDS of as-prepared $\text{Ca}_1\text{Ni}_{0.01}\text{Ti}_{0.99}$, $\text{Ca}_2\text{Ni}_{0.02}\text{Ti}_{0.98}$, and $\text{Ca}_2\text{Ni}_{0.05}\text{Ti}_{0.95}$ are 1.01, 1.01 and 1.09, respectively (Table S1, Supporting Information). All samples showed

$\text{Ca}/(\text{Ni}+\text{Ti})$ higher than 1, excess Ca and Ni exists as CaO and NiO , respectively. All Ni species were incorporated into CaTiO_3 perovskite frameworks in $\text{Ca}_2\text{Ni}_{0.02}\text{Ti}_{0.98}$ MFM as a formation of $\text{Ca}_{1+x}\text{Ni}_y\text{Ti}_{1-y}\text{O}_3/(1-x)\text{CaO}$ without NiO separation. After reduction at 800°C , a very small peak of Ni metal was observed in both $\text{Ca}_2\text{Ni}_{0.02}\text{Ti}_{0.98}$ and $\text{Ca}_2\text{Ni}_{0.05}\text{Ti}_{0.95}$ MFMs (Figure S3b, Supporting Information). Therefore, excess calcium promotes the formation of $\text{Ca}_{1+x}\text{Ni}_y\text{Ti}_{1-y}\text{O}_3$ perovskite with CaO despite the unstable NiO_6 octahedron.

Figure 1c shows XRD patterns between 32.5 to 34° 2theta. The peak of CaTiO_3 perovskite shifts to lower angles from 33.3° (Ca_1Ti_1) to 33.27° (Ca_2Ti_1), indicating volume expansion as the ratio of Ca/Ti increases. According to the Rietveld refinement in

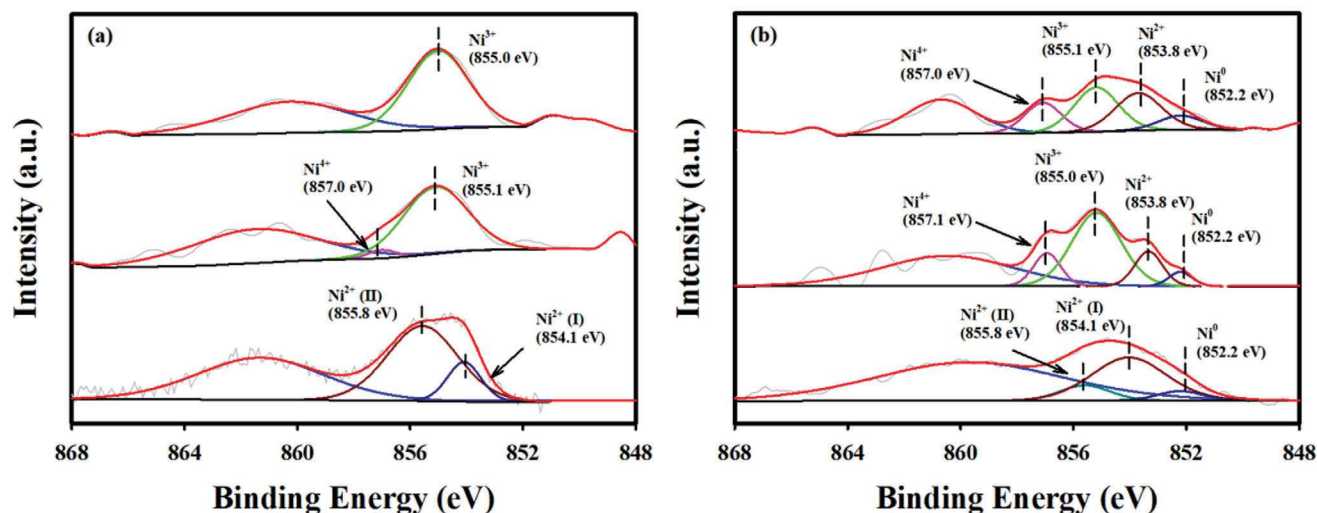


Figure 2. Ni 2p_{3/2} XPS spectra of a) as prepared and b) reduced Ca₂Ni_{0.05}, Ca₂Ni_{0.02}Ti_{0.98} and Ca₂Ni_{0.05}Ti_{0.95}.

Table 1, the lattice parameters of a, b, and c of CaTiO₃ for Ca₁Ti₁ are 5.443, 7.648, and 5.389 Å, respectively. The lattice parameters of a, b, and c for Ca₂Ti₁ are 5.457, 7.658, and 5.402, respectively, which are slightly larger than those of Ca₁Ti₁, leading to volume expansion from 224.32 to 225.76 Å³. Conversely, the diffraction peaks corresponding to CaTiO₃ shifted to a higher angle as the Ni/Ti ratio increased, implying lattice shrinkage owing to the substitution of Ti with Ni.^[21] It was also observed that the lattice parameters of a, b, and c of Ca₂Ni_{0.02}Ti_{0.98} and Ca₂Ni_{0.05}Ti_{0.95} MFMs are smaller than those of Ca₂Ti, and the lattice volume decreased.

X-ray photoelectron spectroscopy (XPS) analysis was conducted for as-prepared and reduced Ca₂Ni_{0.05}, Ca₂Ni_{0.02}Ti_{0.98} and Ca₂Ni_{0.05}Ti_{0.95}. The C-C component peak at 284.8 eV was used to calibrate the XPS raw data (Figure S4, Supporting Information). In the C 1s XPS spectra of all samples, adventitious C-C peak at 284.8 eV and CO₃²⁻ peak at ≈289 eV were observed.^[22] In the sample containing CaO, strong basic site, XPS spectra of CO₃²⁻ peak was high, which might be the CO₂ adsorption in the XPS chamber. In the Ni 2p_{3/2} XPS spectrum of Ca₂Ni_{0.05} DFM, an asymmetric doublet peak of NiO was revealed by the Gaussian-Lorentzian curve fitting, with the peaks located at 8541.1 and 855.8 eV, and a broad satellite peak at higher binding energy at ≈861 eV (Figure 2).^[23] The peak centered at 854.1 eV is attributed to the surface bulk NiO, Ni²⁺(I), whereas the peak at 855.6 eV

is related to the NiO interacting with CaO, Ni²⁺(II).^[4e,24] In literatures, the Ni²⁺(I)/Ni²⁺(II) ratio decreased with an increase in Ca-to-Ni molar ratio in Ni/CaO DFMs.^[4e] For Ca₂Ni_{0.02}Ti_{0.98} and Ca₂Ni_{0.05}Ti_{0.95} MFMs, two different peaks at 857.2 eV and 855.1 eV are attributed to Ni⁴⁺ and Ni³⁺ species, respectively, whereas bulk NiO, Ni²⁺(I), peak was not observed.^[25] Although Ni 2p spectra were unclear because of low Ni amount in the samples, metallic Ni peak at 852.2 eV was observed in all samples after reduction. The Ni⁴⁺ and Ni³⁺ peaks decreased and Ni²⁺ (853.6 eV) and Ni⁰ (852.4 eV) peaks appeared. The existence of Ni⁴⁺ and Ni³⁺ species implies that not all Ni species were exsolved from the host Ca_{1+x}Ni_yTi_{1-y}O₃ perovskite. The detection of Ni²⁺ species implies that Ni⁰ on the surface might be oxidized before measuring XPS results in the chamber.^[23b]

In the Ca 2p XPS spectra of CaO and Ca₂Ni_{0.05} DFM, Ca 2p_{3/2} (350.4 eV) and Ca 2p_{1/2} (346.9 eV) doublet were observed with a separation of 3.5 eV and intensity ratio of 1/2,^[26] and binding energy values remained constant after reduction (Figure 3). For Ca₂Ni_{0.02}Ti_{0.98} and Ca₂Ni_{0.05}Ti_{0.95} MFMs, Ca 2p spectra was deconvoluted into two CaO peaks (350.4 and 346.9 eV) and two CaTiO₃ peaks (349.4 and 345.9 eV).^[27] After reduction, an increase in the ratio of CaO to CaTiO₃ was observed, resulting from the Ni and CaO exsolution from the host Ca_{1+x}Ni_yTi_{1-y}O₃ perovskite.

For Ti 2p XPS spectrum of CaTiO₃, two main distinct peaks were observed at 463.9 and 458.2 eV (Figure 4).^[27] It is clearly seen that the Ti 2p XPS spectra of Ca₂Ni_{0.02}Ti_{0.98} and Ca₂Ni_{0.05}Ti_{0.95} MFMs shifted to lower binding energy after Ni incorporation, and the spectra further shifted with increasing Ni-to-Ti ratio. After reduction, the binding energy values of the MFMs are comparable to that of bare CaTiO₃ perovskite, implying Ni exsolution from the Ca_{1+x}Ni_yTi_{1-y}O₃.

The XPS spectra for O 1s profiles is broad and complicated due to the overlapping peaks of oxygen in lattice of NiO, CaO and CaTiO₃, oxygen defect (oxygen vacancies) and adsorbed oxygen (Figure 5). The O 1s XPS spectrum of CaO contained main peaks located at 531.3 with minor at 532.5 eV, corresponding to lattice oxygen of CaO and adsorbed water or surface hydroxyls

Table 1. Refined cell parameters of Ca₁Ti₁, Ca₂Ti₁, Ca₂Ni_{0.02}Ti_{0.98}, and Ca₂Ni_{0.05}Ti_{0.95} from XRD patterns.

	Quantity (%) CaTiO ₃ /CaO	Lattice parameters (Å)			Lattice volume (Å ³)
		a	b	c	
Ca ₁ Ti ₁	100/—	5.442	7.655	5.387	224.078
Ca ₂ Ti ₁	74/26	5.457	7.658	5.402	225.761
Ca ₂ Ni _{0.02} Ti _{0.98}	70/30	5.446	7.647	5.395	224.655
Ca ₂ Ni _{0.05} Ti _{0.95}	69/31	5.445	7.650	5.399	224.881

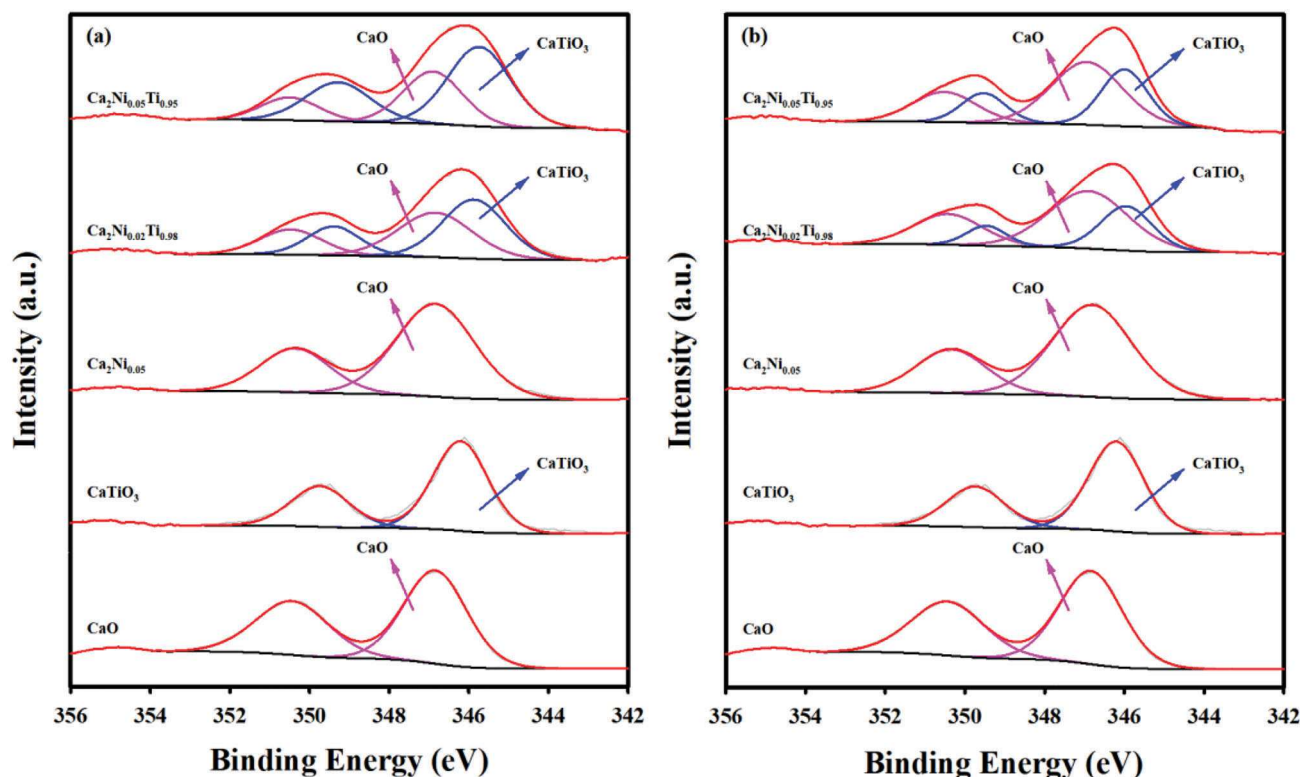


Figure 3. Ca 2p XPS spectra of a) as prepared and b) reduced CaO, CaTiO₃, Ca₂Ni_{0.05}, Ca₂Ni_{0.02}Ti_{0.98} and Ca₂Ni_{0.05}Ti_{0.95}.

on CaO.^[28] In the O 1s XPS spectrum of CaTiO₃, two peaks were deconvoluted at 531.3 and 529.3 eV, which are attributed to adsorbed oxygen in CaTiO₃ and lattice oxygen, respectively.^[27] For Ca₂Ni_{0.05} DFM, two peaks for lattice oxygen of NiO and CaO overlapped at ≈ 531.5 eV, and the peak intensity decreased slightly after reduction, which might be reduction of NiO. Compared to CaTiO₃, a higher peak at ≈ 531.2 eV was observed in Ca₂Ni_{0.02}Ti_{0.98} and Ca₂Ni_{0.05}Ti_{0.95} MFMs, because of CaO exis-

tence. The binding energy of two peaks decreased with increasing Ni ratio. The binding energy values increased after reduction, which are comparable to the spectra of CaO and CaTiO₃. In addition, the ratio of peak (≈ 531.4 eV)-to-peak (≈ 529.1 eV) decreased in the Ca₂Ni_{0.05}Ti_{0.95} MFM after reduction, which might be reduction of NiO on the surface. Based on the XRD and XPS results, it is clearly observed that the incorporated Ni species can be exsolved from the Ca_{1+x}Ni_yTi_{1-y}O₃ perovskite.

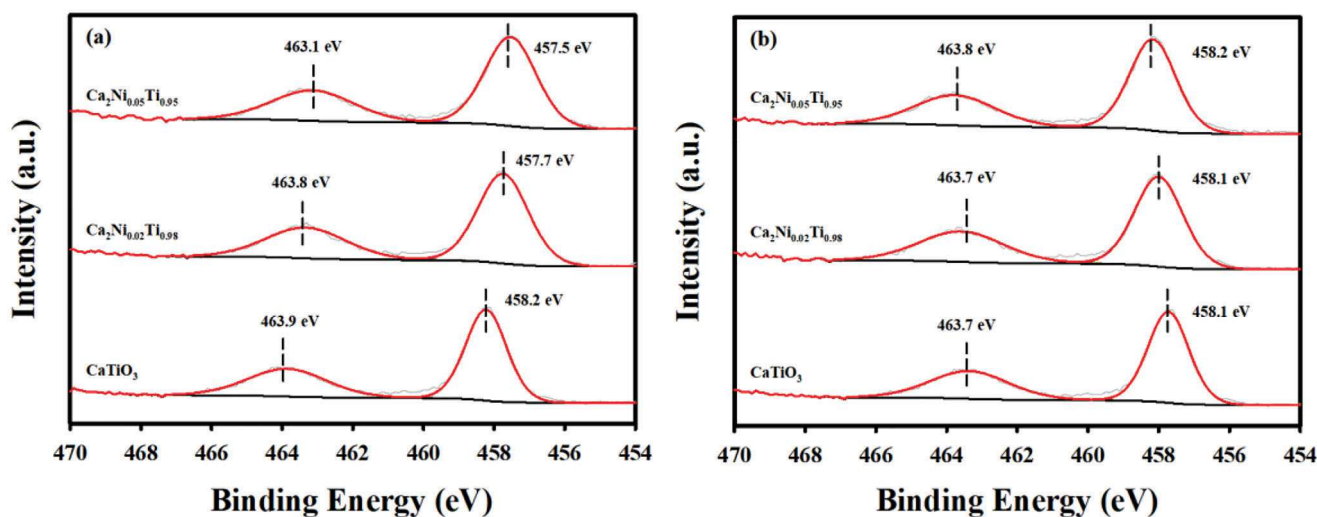


Figure 4. Ti 2p XPS spectra of a) as prepared and b) reduced CaTiO₃, Ca₂Ni_{0.02}Ti_{0.98} and Ca₂Ni_{0.05}Ti_{0.95}.

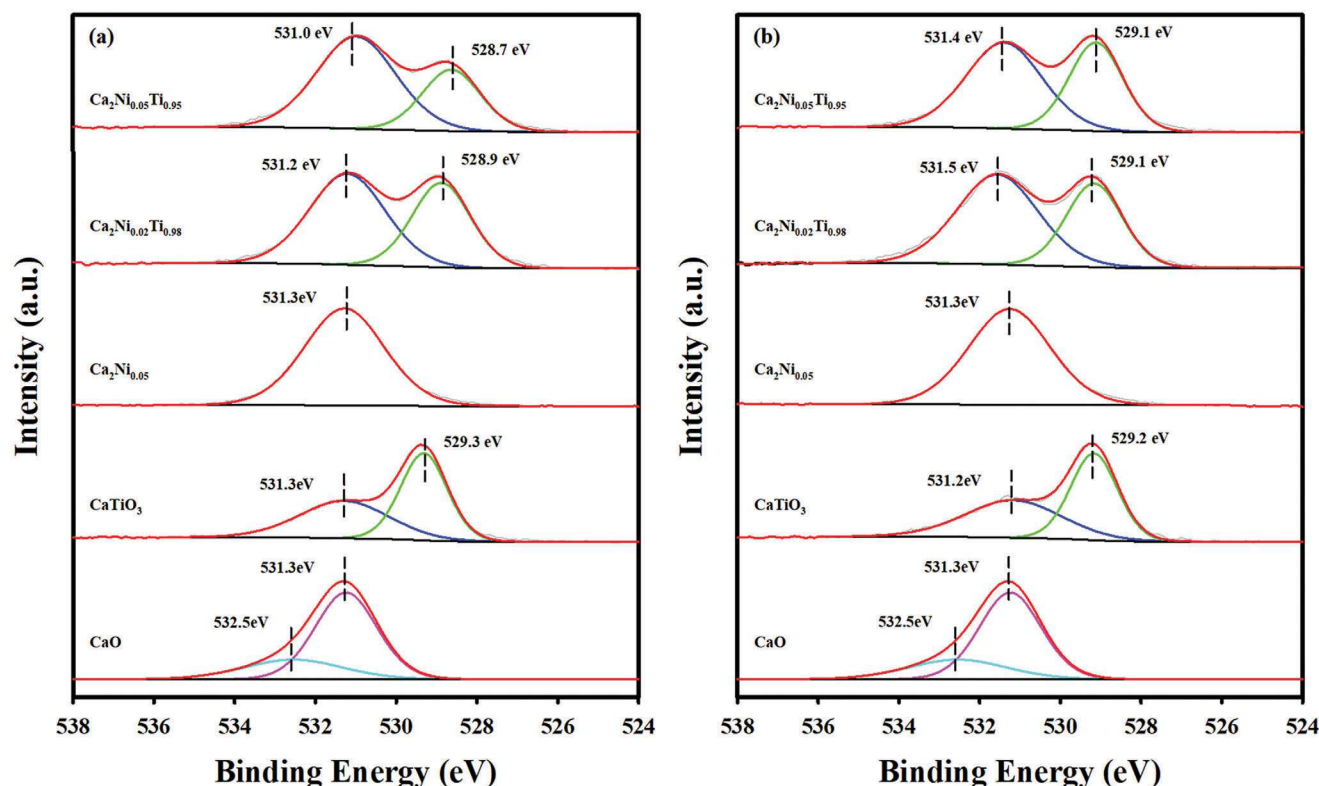


Figure 5. O 1s XPS spectra of a) as prepared and b) reduced CaO, CaTiO₃, Ca₂Ni_{0.05}, Ca₂Ni_{0.02}Ti_{0.98} and Ca₂Ni_{0.05}Ti_{0.95}.

To investigate the self-regeneration properties of Ni (in-situ Ni exsolution from Ca_{1+x}Ni_yTi_{1-y}O₃ and Ni re-dissolving to CaTiO₃ perovskite) under the ICCDRM conditions, Scanning Transmission Electron Microscopy (STEM) High-angle annular dark field imaging (HAADF) experiments with energy-dispersive spectroscopy (EDS) were conducted. Ca₂Ni_{0.02}Ti_{0.98} MFM was selected to observe the self-regeneration of Ni nanoparticles, as no excess NiO species were present on the CaTiO₃ surface in the as-prepared state. The STEM EDS-mapping images of as-prepared Ca₂Ni_{0.02}Ti_{0.98} MFM, cubic/cuboid CaO, and Ca_{1+x}Ni_yTi_{1-y}O₃ perovskite are strongly coupled (Figure 6a). Ni species on the surface of the material were not observed in the as-prepared Ca₂Ni_{0.02}Ti_{0.98} MFM. STEM-EDS images of Ca₂Ni_{0.05} DFM were also measured, and NiO nanoparticles with crystallite size of ≈ 25 nm were unevenly dispersed on the cubic CaO in the STEM EDS-mapping of Ca₂Ni_{0.05} DFM (Figure S5, Supporting Information). Ni nanoparticles (i.e., NiO) with an average crystallite size of ≈ 25 nm were observed in Ca₂Ni_{0.05}Ti_{0.95} MFM (Figure S6, Supporting Information), corresponding to the XRD and XPS results. Although not all Ni nanoparticles are incorporated into CaTiO₃ (i.e., Ca_{1+x}Ni_yTi_{1-y}O₃), they are supported on CaTiO₃ perovskite, which might result in a stronger interaction between Ni and CaTiO₃ than that between Ni and CaO.

After H₂-reduction at 800 °C for 1 h, in situ exsolved Ni nanoparticles were distributed evenly on the surface of CaTiO₃ support (Figure 6b). The Ni nanoparticle size distribution was obtained from the STEM mapping of Ca₂Ni_{0.02}Ti_{0.98} and Ca₂Ni_{0.05}Ti_{0.95} MFMs (Figures S8 and S9, Supporting Information). It is observed in the STEM-HAADF images of

Ca₂Ni_{0.02}Ti_{0.98} MFMs that the Ni nanoparticles are exsolved from Ca_{1+x}Ni_yTi_{1-y}O₃ host perovskite (Figure S7, Supporting Information). For Ca₂Ni_{0.05}Ti_{0.95} MFM, a minority of larger Ni nanoparticles (≈ 23 nm) were observed, as corroborated by XRD, which coexisted with the in-situ exsolved Ni nanoparticles. The average crystallite size of exsolved Ni nanoparticles in Ca₂Ni_{0.02}Ti_{0.98} and Ca₂Ni_{0.05}Ti_{0.95} were 7.06 and 7.48 nm, respectively (Figures S8 and Figure S9, Supporting Information). In the STEM-HAADF image, it is clearly observed that the exsolved Ni nanoparticles were socketed in the host perovskite (Figures S10 and S11, Supporting Information). It is expected that the in-situ exsolved Ni nanoparticles formed from bulk-to-surface diffusion have a stronger interaction with CaTiO₃ and smaller crystallite size than the Ni nanoparticles deposited on the surface of CaTiO₃.

The reduced Ca₂Ni_{0.02}Ti_{0.98} MFM was re-oxidized under CO₂ capture condition (10% CO₂/He condition at 700 °C for 1 h) to investigate the morphology change of exsolved Ni nanoparticles and the composite materials. In the STEM image of Ca₂Ni_{0.02}Ti_{0.98} MFM after re-oxidation with CO₂, the exsolved Ni nanoparticles were dispersed throughout the CaTiO₃ and re-incorporated into the subsurface of CaTiO₃ perovskite (Figure 6c; Figure S12, Supporting Information). Some Ni nanoparticles socketed in the CaTiO₃ perovskite still exist, however, the crystallite size of Ni nanoparticles is much smaller than the exsolved Ni nanoparticles (Figure 6b). The regeneration of larger Ni nanoparticles could have been hindered by the kinetics of re-dissolution, which is an important parameter for predicting the regeneration of exsolved nanoparticles. In addition, CO₂ was chemically absorbed on the CaO grains as a formation of CaCO₃ (Figure S13,

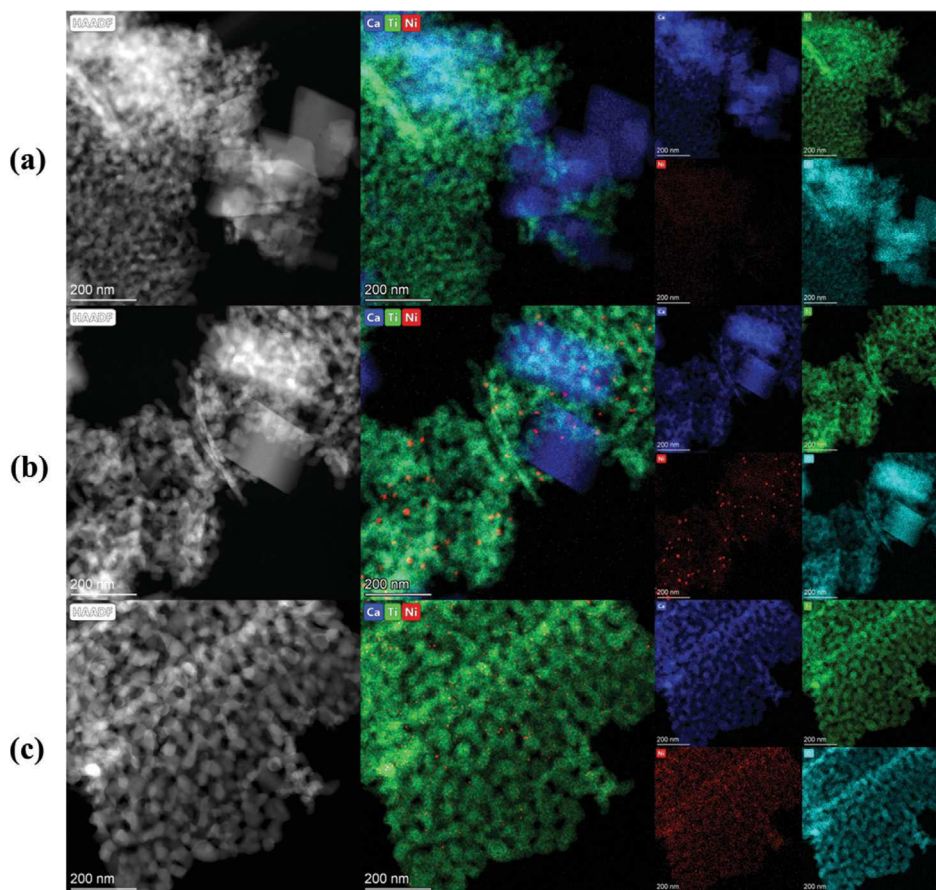


Figure 6. STEM-HAADF images of $\text{Ca}_2\text{Ni}_{0.02}\text{Ti}_{0.98}$ MFM in the states of a) as-prepared, b) reduced by H_2 at 800°C , and c) re-oxidized by CO_2 after CO_2 capture at 700°C .

Supporting Information). It is expected that the volume expansion of CaCO_3 grains by CO_2 capture would not affect Ni exsolution at the subsequent DRM step, because CaCO_3 grains were separated from the host $\text{Ca}_{1+x}\text{Ni}_y\text{Ti}_{1-y}\text{O}_3$ perovskite.

2.2. Enhanced Ni-CaTiO₃ Metal-Support Interaction

Figure 7 shows H_2 -Temperature programmed reduction (H_2 -TPR) results of $\text{Ca}_2\text{Ni}_{0.05}$, $\text{Ca}_2\text{Ni}_{0.02}\text{Ti}_{0.98}$ and $\text{Ca}_2\text{Ni}_{0.05}\text{Ti}_{0.95}$ from 100 to 800°C with temperature ramping of $10^\circ\text{C min}^{-1}$, to investigate metal-support interaction. All samples were pretreated under 20% O_2/He at 800°C for 1 h , to desorb adsorbed gases such as CO_2 and H_2O and to avoid lattice oxygen loss of perovskite. $\text{Ca}_2\text{Ni}_{0.05}$ shows a sharp peak centered at 430°C with shoulder at 455°C , which are attributed to overlapped reduction peak of bulk NiO and NiO interacting with CaO, respectively.^[4e] $\text{Ca}_2\text{Ni}_{0.02}\text{Ti}_{0.98}$ MFM shows one broad peak corresponding to $\text{Ca}_{1+x}\text{Ni}_y\text{Ti}_{1-y}\text{O}_3$ reduction at 450 to 550°C , which is higher than the reduction of bulk NiO. The reduction peak of bulk NiO was not observed, which is consistent with XRD result. $\text{Ca}_2\text{Ni}_{0.05}\text{Ti}_{0.95}$ MFM exhibited two overlapping peaks at 460 and 500°C , respectively. The first reduction peak is ascribed to the reduction of NiO interacting with CaTiO_3 at 460°C . The onset temperature of the first peak is 430°C , which is higher than that of the reduction peak of

bulk NiO (360°C) in the $\text{Ca}_2\text{Ni}_{0.05}$ DFM, implying that NiO interaction with CaTiO_3 is slightly stronger than that with CaO. The second reduction peak at 495°C is attributed to the reduction of

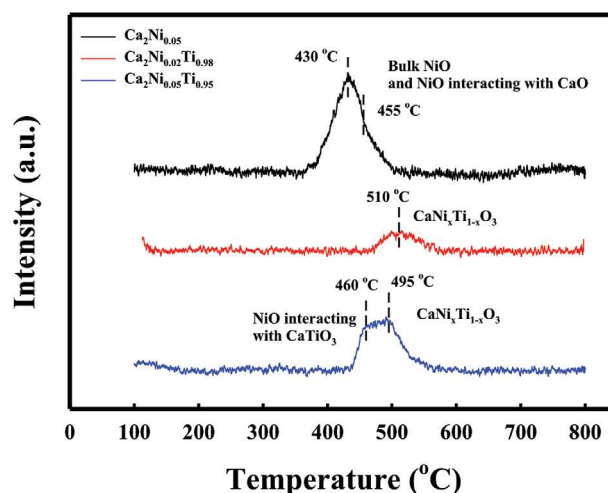


Figure 7. H_2 -TPR profiles of $\text{Ca}_2\text{Ni}_{0.05}$, $\text{Ca}_2\text{Ni}_{0.02}\text{Ti}_{0.98}$, and $\text{Ca}_2\text{Ni}_{0.05}\text{Ti}_{0.95}$ under $10\text{ vol}\%$ H_2 from 100 to 800°C .

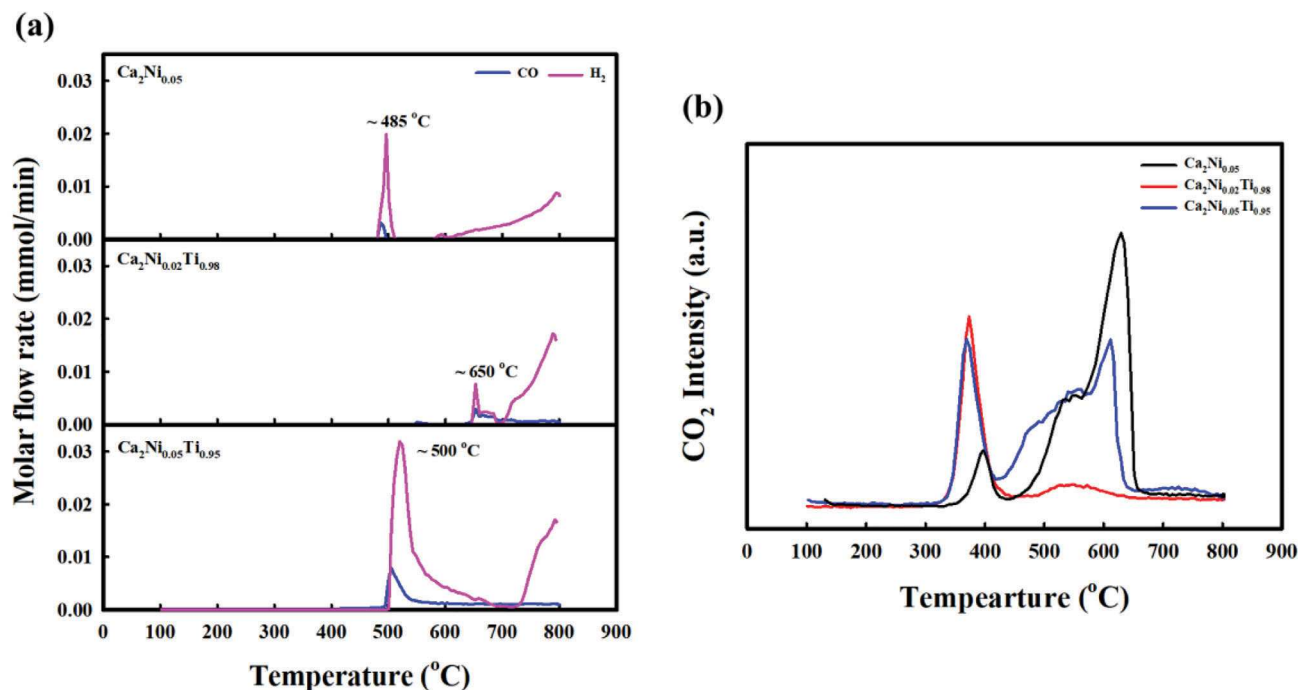


Figure 8. a) CH₄-TPR under 10 vol% CH₄ from 100 to 800 °C and b) TPO after CH₄-treatment at 800 °C for 1 h over Ca₂Ni_{0.05}, Ca₂Ni_{0.02}Ti_{0.98}, and Ca₂Ni_{0.05}Ti_{0.95}.

Ca_{1+x}Ni_yTi_{1-y}O₃ reduction, which is lower slightly than that in the Ca₂Ni_{0.02}Ti_{0.98} MFM.

To investigate the metal support interaction between Ni nanoparticles socketed in CaTiO₃ and reaction performance over reduced Ni under CH₄ condition, CH₄-TPR tests of Ca₂Ni_{0.05}, Ca₂Ni_{0.02}Ti_{0.98}, and Ca₂Ni_{0.05}Ti_{0.95} were conducted in the presence of 10 vol% CH₄ from 100 to 800 °C with temperature ramping of 10 °C min⁻¹ (Figure 8a). All samples were pre-treated under 20 vol% O₂/He at 800 °C for 1 h to desorb gases such as CO₂ and H₂O and to avoid oxygen loss in the CaTiO₃ lattice for Ca₂Ni_{0.02}Ti_{0.98} and Ca₂Ni_{0.05}Ti_{0.95}. CH₄ partial oxidation (POx), MeOx(s) + CH₄(g) ↔ MeOx-δ(x) + CO(g) + 2H₂(g), is accompanied by Ni species (NiO or Ca_{1+x}Ni_yTi_{1-y}O₃) reduction. In-situ exsolution of Ni nanoparticles was also observed after CH₄-treatment at 800 °C for 1 h over the Ca₂Ni_{0.02}Ti_{0.98} and Ca₂Ni_{0.05}Ti_{0.95} MFMs in STEM-EDS mapping (Figure S14, Supporting Information). The onset temperatures of CH₄ POx over Ca₂Ni_{0.05}, Ca₂Ni_{0.02}Ti_{0.98}, and Ca₂Ni_{0.05}Ti_{0.95} are ≈485, ≈650, and ≈500 °C, respectively. CH₄ POx at low temperatures (485 – 550 °C) is attributed to NiO reduction for Ca₂Ni_{0.05} and Ca₂Ni_{0.05}Ti_{0.95}, whereas CH₄ POx at ≈650 °C is ascribed to Ni species reduction in Ca_{1+x}Ni_yTi_{1-y}O₃ perovskite for Ca₂Ni_{0.02}Ti_{0.98}. For Ca₂Ni_{0.05}Ti_{0.95} MFM, onset temperature of CH₄ POx by reduction of NiO (≈500 °C) is slightly higher than that of NiO species in Ca₂Ni_{0.05} DFM (485 °C), NiO(s) + CH₄(g) ↔ Ni⁰(s) + CO(g) + 2H₂(g), because the interaction between Ni and CaTiO₃ in Ca₂Ni_{0.05}Ti_{0.95} MFM is stronger than that between Ni and CaO in Ca₂Ni_{0.05} DFM. In addition, the broad H₂ peaks (550 – 700 °C) are attributed to the reduction of Ca_{1+x}Ni_yTi_{1-y}O₃. For Ca₂Ni_{0.02}Ti_{0.98} MFM, the reduction of Ca_{1+x}Ni_yTi_{1-y}O₃ between 650 and 700 °C, Ca_{1+x}Ni_yTi_{1-y}O_{3-δ}(s) + βCH₄(g) ↔ αNi⁰ + αCaO +

Ca_{1+x-α}Ni_{y-α}Ti_{1-y}O_{3-δ}(s) + βCO(s) + 2βH₂(g), is much higher than that for Ca₂Ni_{0.05}Ti_{0.95} MFM. After H₂ reduction of Ca₂Ni_{0.02}Ti_{0.98} MFM, CH₄ POx by the reduction of Ca_{1+x}Ni_yTi_{1-y}O₃ was not observed during the CH₄-TPSR (Figure S15, Supporting Information). It is assumed that NiO on the surface of CaTiO₃ in the Ca₂Ni_{0.05}Ti_{0.95} MFM was reduced first by CH₄ (≈500 °C), and then products (CO and H₂) as reducing gases promoted Ni species reduction in the Ca_{1+x}Ni_yTi_{1-y}O₃ (550 – 700 °C). Notably, the interaction between Ni species and support materials is as follows: Ca₂Ni_{0.02}Ti_{0.98} >> Ca₂Ni_{0.05}Ti_{0.95} > Ca₂Ni_{0.05}.

After NiO reduction, H₂ was produced over Ca₂Ni_{0.05} DFM at temperatures higher than 600 °C, which is CH₄ decomposition over reduced Ni, CH₄(g) ↔ C(s) + 2H₂(g). In contrast, for Ca₂Ni_{0.02}Ti_{0.98} and Ca₂Ni_{0.05}Ti_{0.95} MFMs, H₂ gases were produced above 700 °C, which is accompanied by CO production from in situ coke gasification by CaTiO₃, CaTiO₃(s) + C(s) ↔ CaTiO_{3-δ}(s) + δCO(g). Although the Ca₂Ni_{0.05} DFM was reduced at lower temperatures, CH₄ decomposition activity at 800 °C is lower than that of Ca₂Ni_{0.02}Ti_{0.98} and Ca₂Ni_{0.05}Ti_{0.95} MFMs because of poor Ni dispersion (Table S2, Supporting Information). This phenomenon was also observed in the CH₄-TPR of the bare CaTiO₃ perovskite (Ca₁Ti₁), making CO and H₂ at temperatures higher than 600 °C (Figure S16, Supporting Information).

Figure 8b shows the temperature programmed oxidation (TPO) profiles of Ca₂Ni_{0.05}, Ca₂Ni_{0.02}Ti_{0.98}, and Ca₂Ni_{0.05}Ti_{0.95} after CH₄ treatment at 800 °C for 1 h. It is widely recognized that the temperature of coke combustion is highly dependent on its location and properties. A lower combustion temperature of the deposited coke leads to increased oxygenation, while proximity to the active site catalyzes combustion. Closer proximity of coke to catalysts is usually observed in the form of encapsulating

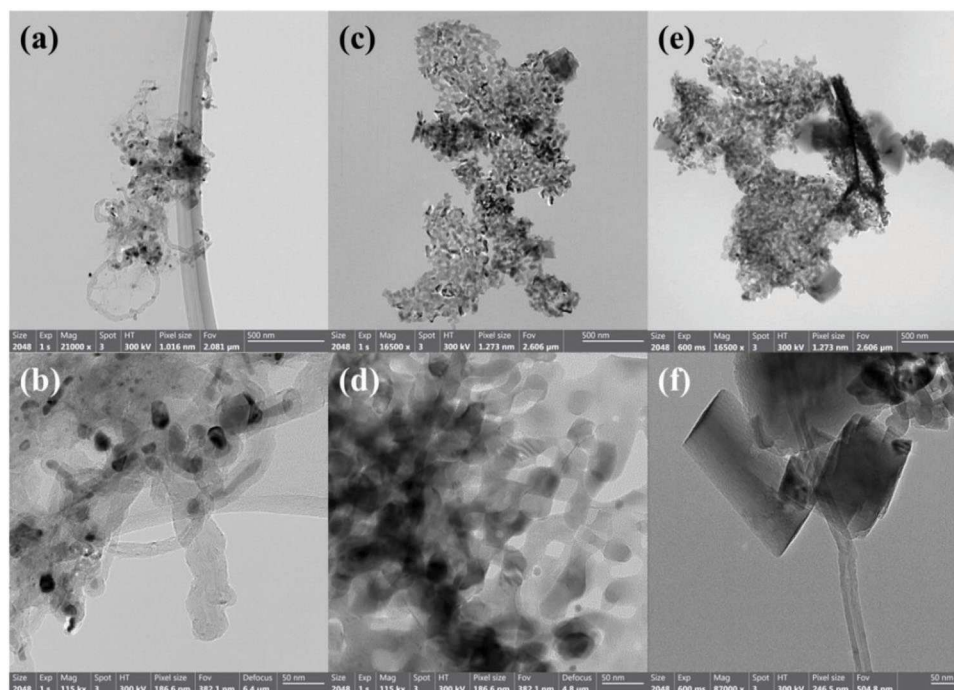


Figure 9. HRTEM images of a,b) $\text{Ca}_2\text{Ni}_{0.05}$, c,d) $\text{Ca}_2\text{Ni}_{0.02}\text{Ti}_{0.98}$, and e,f) $\text{Ca}_2\text{Ni}_{0.05}\text{Ti}_{0.95}$ after CH_4 -treatment under 10 vol% CH_4/He at 800 °C for 1 h.

coke, whereas filamentous coke is located away from the metallic sites. Three different types of CO_2 peaks can be identified in the TPO profiles for $\text{Ca}_2\text{Ni}_{0.05}$, $\text{Ca}_2\text{Ni}_{0.02}\text{Ti}_{0.98}$, and $\text{Ca}_2\text{Ni}_{0.05}\text{Ti}_{0.95}$ at 300 – 400 °C (Type I), 400 – 600 °C (Type II) and 550 – 650 °C (Type III).^[8] The peaks at lower temperatures (Type I) correspond to the combustion of a non-filamentous or encapsulating coke closer to the active sites catalyzing coke combustion. The peaks at higher temperatures (Type II) are ascribed to the filamentous coke between the catalysts and support materials, which have grown from the catalyst's surface. However, the Type III CO_2 peaks are assumed to be the desorption of CO_2 captured by CaO at lower temperatures during the TPO because there is no O_2 consumption in this range (Figure S17, Supporting Information). $\text{Ca}_2\text{Ni}_{0.05}$ DFM shows a small amount of Type I coke combustion at ≈ 400 °C and a higher fraction of overlapped Type II and III CO_2 peaks at temperatures between 450 and 650 °C, indicating filamentous coke deposition. Noticeable filamentous coke was observed between Ni and CaO in high-resolution transmission spectroscopy (HRTEM) in (Figure 9a,b). For $\text{Ca}_2\text{Ni}_{0.02}\text{Ti}_{0.98}$ MFM, non-filamentous coke combustion (Type I) between 330 and 450 °C and small peaks of filamentous coke combustion (Type II) between 500 and 600 °C were observed. Filamentous coke is less likely to be deposited between exsolved Ni nanoparticles and CaTiO_3 due to the submerged interaction with the perovskite oxide, and filamentous coke deposition was observed in $\text{Ca}_2\text{Ni}_{0.02}\text{Ti}_{0.98}$ MFM (Figure 9c,d). Although the intensity of type I coke combustion for $\text{Ca}_2\text{Ni}_{0.02}\text{Ti}_{0.98}$ and $\text{Ca}_2\text{Ni}_{0.05}\text{Ti}_{0.95}$ MFMs are comparable, $\text{Ca}_2\text{Ni}_{0.05}\text{Ti}_{0.95}$ MFM exhibited higher CO_2 intensity of type II and III because larger Ni nanoparticles coexisted with in-situ exsolved smaller Ni nanoparticles in $\text{Ca}_2\text{Ni}_{0.05}\text{Ti}_{0.95}$ MFM. Compared to $\text{Ca}_2\text{Ni}_{0.05}$ DFM, the Type II coke in $\text{Ca}_2\text{Ni}_{0.05}\text{Ti}_{0.95}$ MFM was gasified at lower temperatures, meaning closer prox-

imity of Ni nanoparticles to coke deposited. A small amount of filamentous coke between Ni and CaTiO_3 perovskite was observed (Figure 9e,f). Despite the higher CH_4 decomposition activity, smaller size of Ni nanoparticles, strong interactions between socketed Ni and host CaTiO_3 perovskite, and lattice oxygen of CaTiO_3 in the $\text{Ca}_2\text{Ni}_{0.02}\text{Ti}_{0.98}$ MFM could alleviate the filamentous coke deposition during the ICCDRM at lower temperature (700 °C). It is also expected that the deposited coke on the surface of Ni nanoparticles (Type I) during the DRM step is likely to be gasified by CO_2 to CO during the subsequent CO_2 capture step, $\text{C(s)} + \text{CO}_2(\text{g}) \leftrightarrow 2\text{CO(g)}$.

2.3. ICCDRM Performance

CH_4 -TPSR after CO_2 capture was conducted over $\text{Ca}_2\text{Ni}_{0.02}\text{Ti}_{0.98}$ MFM to determine the optimal reaction temperature for the ICCDRM process (Figure 10a). Prior to CH_4 -TPSR, the $\text{Ca}_2\text{Ni}_{0.02}\text{Ti}_{0.98}$ MFM was carbonated under 10 vol% CO_2/He condition at 700 °C for 1 h. The onset temperature of CO_2 desorption was observed at ≈ 620 °C during the TPD under pure He condition (Figure S18, Supporting Information). As expected, the re-incorporated Ni species ($\text{Ca}_{1-x}\text{Ni}_x\text{Ti}_{1-y}\text{O}_{3-\delta}$ phase) during the CO_2 capture step can be reduced at ≈ 680 °C, which is accompanied by CH_4 $\text{POx Ca}_{1-x}\text{Ni}_y\text{Ti}_{1-y}\text{O}_{3-\delta}/(1-x)\text{CaCO}_3(\text{s}) + (\beta+1-x)\text{CH}_4(\text{g}) \leftrightarrow \alpha\text{Ni}^0/\text{Ca}_{1-x}\text{Ni}_{y-\alpha}\text{Ti}_{1-y}\text{O}_{3-\delta}(\text{s}) + (\beta+1-x)\text{CO(g)} + 2(\beta+1-x)\text{H}_2(\text{g})$ as mentioned above. Then, the desorbed CO_2 and CH_4 reacted to syngas (CO and H_2) via DRM over metallic Ni between 680 and 720 °C, $\text{CO}_2(\text{g}) + \text{CH}_4(\text{g}) \leftrightarrow 2\text{CO(g)} + 2\text{H}_2(\text{g})$. During the DRM, the desorbed CO_2 reacts with H_2 produced from DRM to CO , $\text{CO}_2(\text{g}) + \text{H}_2(\text{g}) \leftrightarrow \text{CO(g)} + \text{H}_2\text{O(g)}$, leading to the decrease in H_2/CO ratio (below 1). After the complete DRM reaction, CH_4

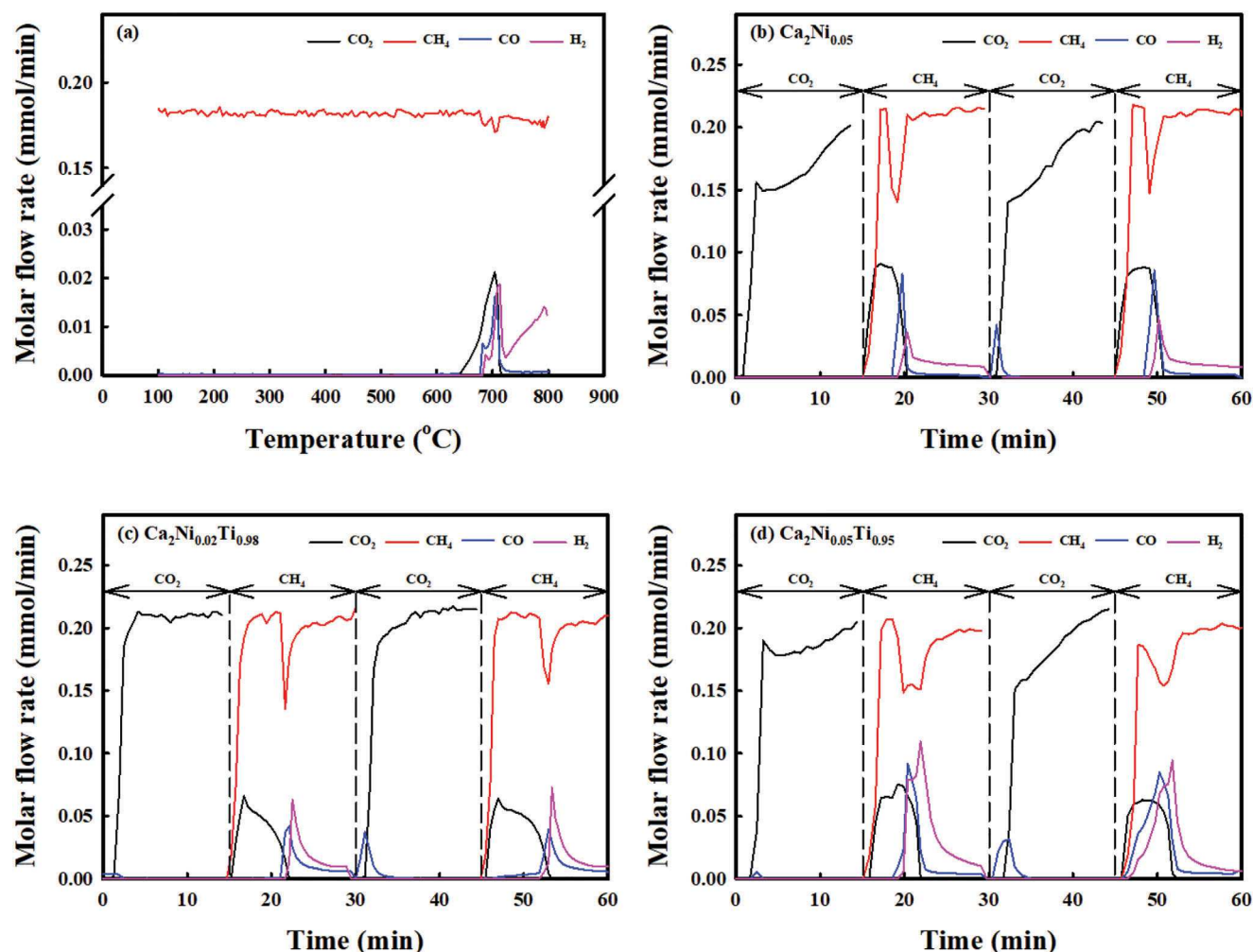


Figure 10. a) CH₄-TPSR after CO₂ capture under 10 vol% CH₄/He condition from 100 to 800 °C over Ca₂Ni_{0.02}Ti_{0.98} MFM. CO₂ breakthrough curves and DRM profiles of b) Ca₂Ni_{0.05}, c) Ca₂Ni_{0.02}Ti_{0.98}, and d) Ca₂Ni_{0.05}Ti_{0.95} in the first 2 cycles of ICCDRM at 700 °C (carbonation: 10 vol% CO₂/He and DRM: 10 vol% CH₄/He).

decomposed to coke and H₂, CH₄(g) ↔ C(s) + 2H₂(g), and the H₂ productivity increased with reaction temperature. During the ICCDRM over Ca₂Ni_{0.02}Ti_{0.98} MFM at 650 °C, syngas was not produced for 30 min (Figure S19, Supporting Information). The performance, such as CO₂ capture and syngas production of the MFMs in the ICCDRM, was investigated during the 30 cycles of CO₂ and CH₄ streams at 700 °C. To study the redox properties of Ni species and consecutive reactions under CO₂ and CH₄ conditions, the ICCDRM process was conducted with high WHSV (60 000 ml g⁻¹ h⁻¹). Figure 5b–d shows the CO₂ breakthrough curves and DRM profiles of Ca₂Ni_{0.05}, Ca₂Ni_{0.02}Ti_{0.98}, and Ca₂Ni_{0.05}Ti_{0.95} in the first 2 cycles of ICCDRM and overall reactions occurred at each step (H₂ reduction, CO₂ capture, and DRM) in the ICCDRM are summarized in Table S3 (Supporting Information). Before the CO₂ capture step, all samples were reduced under 5 vol% H₂/He at 800 °C for 1 h, and then the temperature decreased to 700 °C under He condition. During the CO₂ capture step (10 vol% CO₂/He stream), the molar flow rate of outlet CO₂ was lower than that of inlet CO₂ at the beginning of the reaction because of CO₂ capture by CaO to form CaCO₃,

CaO(s) + CO₂(g) ↔ CaCO₃(g). In addition to the CO₂ capture by CaO, reoxidation of metallic Ni into NiO and Ca_{1+x}Ni_yTi_{1-y}O₃ was accompanied by small amount of CO production; Ni⁰(s) + CO₂(g) ↔ NiO(s) + CO(g) for Ca₂Ni_{0.05} and Ca₂Ni_{0.05}Ti_{0.95}, and αNi⁰/Ca_{1+x}Ni_yTi_{1-y}O_{3-δ}(s) + βCO₂(g) ↔ Ca_{1+x}Ni_yTi_{1-y}O_{3-δ}(s) + βCO(g) for Ca₂Ni_{0.02}Ti_{0.98} and Ca₂Ni_{0.05}Ti_{0.95}. XRD results also confirmed that most of the CaO in all samples was converted into CaCO₃ at 700 °C and Ni⁰ peak disappeared after carbonation (Figure S20a,b, Supporting Information).

During the subsequent DRM step (10 vol% CH₄/He stream), the CO₂ was desorbed from CaCO₃, and the molar flow rate of outlet CH₄ initially reached that of inlet CH₄ because of the high WHSV, as mentioned above. CH₄ reacted with the desorbed CO₂ to CO and H₂ over metallic Ni, CO₂(g) + CH₄(g) ↔ 2CO(g) + 2H₂(g). The time when the highest CH₄ conversion was achieved for Ca₂Ni_{0.05}, Ca₂Ni_{0.02}Ti_{0.98}, and Ca₂Ni_{0.05}Ti_{0.95} are 19.2, 21.6, 19.8 min, respectively, which has inversely proportional to the interaction between Ni species and support materials (Ca₂Ni_{0.02}Ti_{0.98} >> Ca₂Ni_{0.05}Ti_{0.95} > Ca₂Ni_{0.05}), as stated in Figure 3a. This is because the NiO supported on CaO (Ca₂Ni_{0.05})

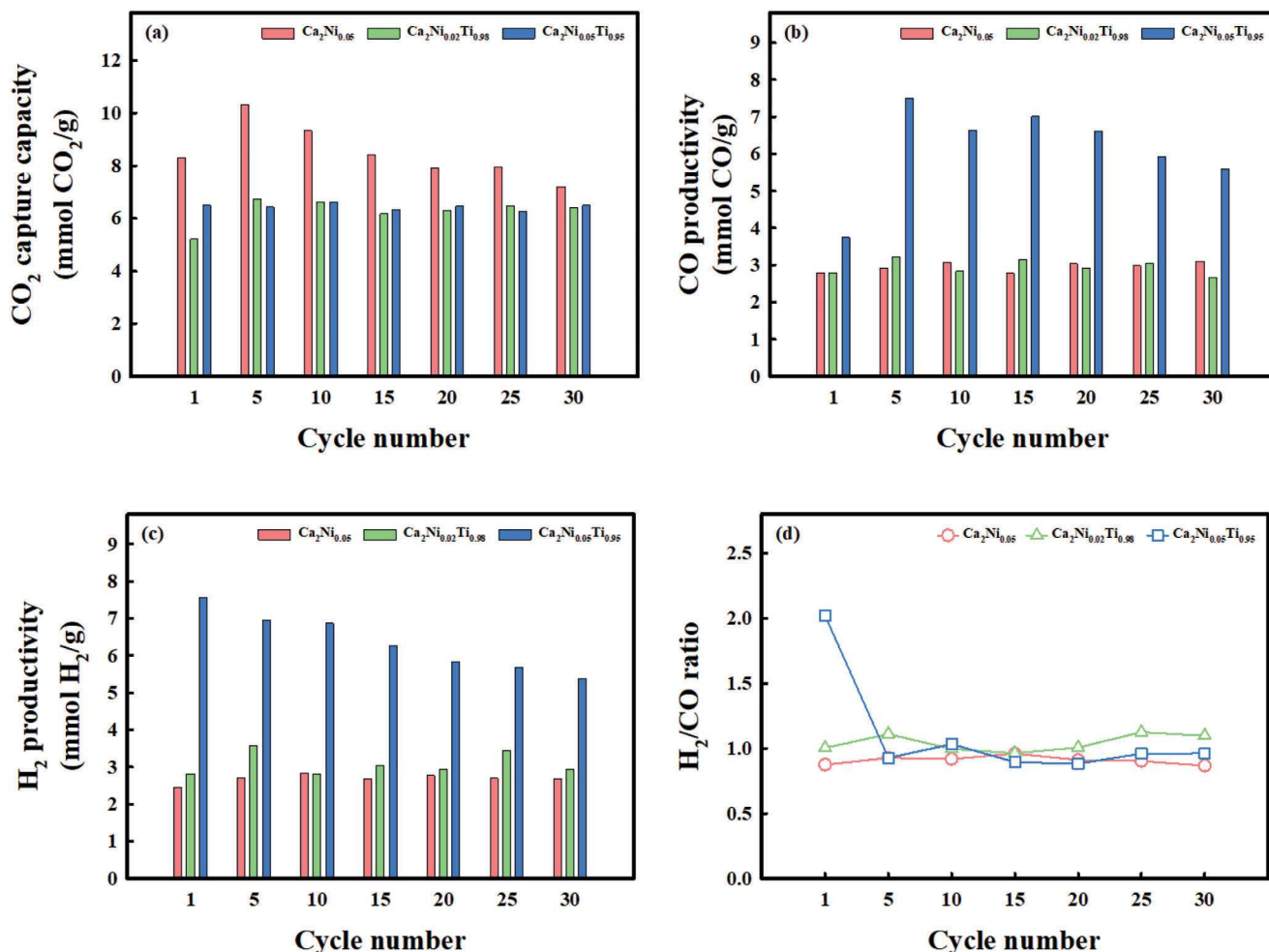


Figure 11. a) CO_2 capture capacity, b) CO productivity, c) H_2 productivity, and d) H_2/CO ratio of $\text{Ca}_2\text{Ni}_{0.05}$, $\text{Ca}_2\text{Ni}_{0.02}\text{Ti}_{0.98}$, and $\text{Ca}_2\text{Ni}_{0.05}\text{Ti}_{0.95}$ during 30 cycles of ICCDRM at 700 °C (CO_2 capture: 10 vol% CO_2/He and DRM: 10 vol% CH_4/He).

or CaTiO_3 ($\text{Ca}_2\text{Ni}_{0.05}\text{Ti}_{0.95}$) were reduced fast, compared to the $\text{Ca}_{1+x}\text{Ni}_y\text{Ti}_{1-y}\text{O}_3$ in $\text{Ca}_2\text{Ni}_{0.02}\text{Ti}_{0.98}$. Therefore, more desorbed CO_2 can be converted via DRM or rWGS reactions in the $\text{Ca}_2\text{Ni}_{0.05}$ and $\text{Ca}_2\text{Ni}_{0.05}\text{Ti}_{0.95}$, compared to $\text{Ca}_2\text{Ni}_{0.02}\text{Ti}_{0.98}$. The H_2/CO ratio at the highest CH_4 conversion is below 1 because desorbed CO_2 reacts with H_2 produced from DRM to produce CO via rWGS, $\text{CO}_2(\text{g}) + \text{H}_2(\text{g}) \leftrightarrow \text{CO}(\text{g}) + \text{H}_2\text{O}(\text{g})$. In addition to the DRM reaction, CH_4 decomposed to coke and H_2 , $\text{CH}_4(\text{g}) \leftrightarrow \text{C}(\text{s}) + 2\text{H}_2(\text{g})$, after complete CO_2 desorption. For $\text{Ca}_2\text{Ni}_{0.02}\text{Ti}_{0.98}$ and $\text{Ca}_2\text{Ni}_{0.05}\text{Ti}_{0.95}$ MFMs, the deposited coke was in-situ gasified by lattice oxygen in CaTiO_3 .

At the 2nd CO_2 capture step, in addition to the Ni species oxidation, coke deposited during the 1st DRM step was gasified by CO_2 to CO via reverse Boudouard reaction at the beginning of the reaction, $\text{C}(\text{s}) + \text{CO}_2(\text{g}) \leftrightarrow 2\text{CO}(\text{g})$. Therefore, the CO produced at the 2nd CO_2 capture is significantly higher than at the 1st cycle. At the 2nd DRM step, $\text{Ca}_2\text{Ni}_{0.05}$ DFM exhibited similar results to the first DRM step. For the $\text{Ca}_2\text{Ni}_{0.02}\text{Ti}_{0.98}$ MFM, a small amount of CO gas was produced at the beginning of the reaction (48–50 min). This phenomenon is assumed that $\text{Ca}_{1+x}\text{Ni}_y\text{Ti}_{1-y}\text{O}_3$ was reduced by CH_4 to make CO and H_2 , $\text{Ca}_{1+x}\text{Ni}_y\text{Ti}_{1-y}\text{O}_{3-\delta}(\text{s})$

+ $\beta\text{CH}_4(\text{g}) \leftrightarrow \alpha\text{Ni}^0/\text{Ca}_{1+x-\alpha}\text{Ni}_{y-\alpha}\text{Ti}_{1-y}\text{O}_{3-\delta}(\text{s}) + \beta\text{CO}(\text{g}) + 2\beta\text{H}_2(\text{g})$. Then the produced H_2 reacts subsequently with desorbed CO_2 to CO via rWGS, $\text{CO}_2(\text{g}) + \text{H}_2(\text{g}) \leftrightarrow \text{CO}(\text{g}) + \text{H}_2\text{O}(\text{g})$. This implies that the partially re-incorporated Ni nanoparticles during the rapid CO_2 capture step were easily reduced under the CH_4 stream compared to the 1st cycles. $\text{Ca}_2\text{Ni}_{0.05}\text{Ti}_{0.95}$ MFM exhibited a notable increase in CO and H_2 production at the beginning of the reaction (46–50 min). In the XRD results after the DRM step, all CaCO_3 converted to CaO and small Ni^0 peak appeared after 30 cycles of ICCDRM (Figure S20c,d, Supporting Information).

Figure 11 exhibited CO_2 capture capacity, syngas (CO and H_2) productivity, and H_2/CO ratio of $\text{Ca}_2\text{Ni}_{0.05}$, $\text{Ca}_2\text{Ni}_{0.02}\text{Ti}_{0.98}$, and $\text{Ca}_2\text{Ni}_{0.05}\text{Ti}_{0.95}$ during 30 cycles of ICCDRM at 700 °C to compare the CO_2 capture efficiency, catalytic activity, and deactivation properties during cyclic tests. CO_2 capture capacity and syngas productivity were calculated from the CO_2 breakthrough curves and DRM profiles, respectively. H_2/CO ratio is calculated from the overall CO and H_2 productivity during the DRM step. At the 1st cycle, CO_2 capture capacity of $\text{Ca}_2\text{Ni}_{0.05}$, $\text{Ca}_2\text{Ni}_{0.02}\text{Ti}_{0.98}$, and $\text{Ca}_2\text{Ni}_{0.05}\text{Ti}_{0.95}$ were 8.28, 5.19 and 6.49 mmol CO_2/g ,

respectively. $\text{Ca}_2\text{Ni}_{0.05}$ DFM showed the highest CO_2 capture capacity because of its higher CaO content without CaTiO_3 , compared to the $\text{Ca}_2\text{Ni}_{0.02}\text{Ti}_{0.98}$ and $\text{Ca}_2\text{Ni}_{0.05}\text{Ti}_{0.95}$ MFMs. CO_2 capture capacity of $\text{Ca}_2\text{Ni}_{0.05}$ DFM increased to 10.3 mmol CO_2/g due to the morphology change of CaO/CaCO_3 molecules during the 1st cycle of ICCDRM. Then, it decreased gradually to 7.19 mmol CO_2/g because of the thermal sintering of CaO. The crystallite size of CaO increased from 28.5 to 47.9 nm after 30 cycles of ICCDRM at 700 °C (Table S4, Supporting Information). On the other hand, $\text{Ca}_2\text{Ni}_{0.02}\text{Ti}_{0.98}$ and $\text{Ca}_2\text{Ni}_{0.05}\text{Ti}_{0.95}$ MFMs exhibited stable CO_2 capture capacity during the 30 cycles of ICCDRM at 700 °C. This is because the CaTiO_3 acted as a physical barrier intra-region of CaO/CaCO_3 molecules, which alleviated the thermal sintering of CaO. The crystallite size of CaO in $\text{Ca}_2\text{Ni}_{0.02}\text{Ti}_{0.98}$ and $\text{Ca}_2\text{Ni}_{0.05}\text{Ti}_{0.95}$ MFM increased slightly after 30 cycles of ICCDRM at 700 °C ($\text{Ca}_2\text{Ni}_{0.02}\text{Ti}_{0.98}$: 28.1 to 29.9 nm and $\text{Ca}_2\text{Ni}_{0.05}\text{Ti}_{0.95}$: 24.7 to 31.2 nm).

During the subsequent DRM, syngas productivity of $\text{Ca}_2\text{Ni}_{0.05}$ DFM increased slightly during the 30 cycles (CO : 3.26 – 3.61 mmol CO/g and H_2 : 2.41 – 2.65 mmol H_2/g) because of higher CO_2 capture capacity than that at the 1st cycle. However, the overall H_2/CO ratio decreased slightly from 0.87 to 0.73, resulting from decreased CH_4 decomposition because of severe coke accumulation with cycles. After 30 cycles of ICCDRM, severe Ni nanoparticle sintering and filamentous coke deposition between Ni and large-size nanoparticles were observed in STEM-EDS images (Figure S21, Supporting Information). Coke-encapsulating Ni nanoparticles were not observed in the HRTEM image. For $\text{Ca}_2\text{Ni}_{0.02}\text{Ti}_{0.98}$ MFM, syngas (CO and H_2) productivity increased slightly, and the H_2/CO ratio was maintained from 0.96 to 1.12. After 30 cycles of ICCDRM at 700 °C, the crystallite size of Ni measured by STEM-EDS images is comparable to that of the freshly reduced samples (Figure S22, Supporting Information). A very thin layer of coke encapsulating Ni nanoparticles was observed in the HRTEM image. For $\text{Ca}_2\text{Ni}_{0.05}\text{Ti}_{0.95}$ MFM, CO productivity at the 1st cycle is 3.74 mmol CO/g and increased to 7.49 mmol CO/g at the 5th cycle because of the increase in CO production at the beginning of the DRM step, as mentioned above. CO productivity decreased gradually to 5.58 mmol CO/g after the 5th cycle. H_2 productivity gradually reduced from 7.56 to 5.37 mmol H_2/g during the 30 cycles. As mentioned above, the H_2/CO ratio at the 1st cycle is 2.02 and then reduced to 0.88 – 1.03 because of a significant increase in CO production. Ni nanoparticle sintering was not observed in the STEM-EDS images after 30 cycles of ICCDRM (Figure S23, Supporting Information). In the HRTEM image of $\text{Ca}_2\text{Ni}_{0.05}\text{Ti}_{0.95}$ MFM after 30 cycles of ICCDRM, coke encapsulating Ni nanoparticles were observed on the Ni with small crystallite size (≈ 8 nm) that is strongly adhered to the CaTiO_3 perovskite (Figure S23c, Supporting Information). Figure S23d (Supporting Information) shows Ni encapsulated by a thick layer of coke with larger crystallites (≈ 20 nm) and filamentous coke between Ni and CaTiO_3 .

To prove the self-regeneration properties (Ni exsolution and re-incorporation) of Ni-doped $\text{CaTiO}_3/\text{CaO}$ MFM, XPS spectra measurements were conducted after ICCDRM reactions (Figure S24, Supporting Information). Although Ni XPS spectra were unclear due to the low Ni amount in the sample, it was observed that Ni^0 peak appeared after reduction decreased after carbonation step, and then Ni^0 peak appeared again after the 1st and 30th DRM

steps. During the self-regeneration, not all Ni species were exsolved and some parts of Ni species existed as $\text{Ni}^{4+}/\text{Ni}^{3+}$ in the $\text{Ca}_{1+x}\text{Ni}_y\text{Ti}_{1-y}\text{O}_3$ perovskite. In the Ca 2p spectra, CaO-to- CaTiO_3 ratio increased after reduction due to the exsolution of CaO, and then decreased after carbonation step, which was accompanied by Ni re-incorporation. After DRM step, CaO-to- CaTiO_3 ratio decreased. In the Ti 2p spectra, binding energy values of $\text{Ca}_2\text{Ni}_{0.02}\text{Ti}_{0.98}$ MFM were lower than those of CaTiO_3 , as mentioned above (Figure 4). After reduction, Ti 2p peaks shifted to higher binding energy, which is comparable to that of CaTiO_3 . The Ti 2p peaks decreased after carbonation, and then increased after DRM step. In the O 1s spectra, a new peak was observed at ≈ 533 eV after carbonation step, which might be absorbed CO_2 by CaO (CO_3^{2-}). However, the peak at ≈ 533 eV was still observed after DRM steps. Considering complete conversion of CaCO_3 to CaO in the XRD result, the peak might be attributed to active CHx during DRM step.^[29] Based on the XRD, XPS and STEM results, it is concluded that the exsolved Ni nanoparticles from the $\text{Ca}_{1+x}\text{Ni}_y\text{Ti}_{1-y}\text{O}_3$ can be re-incorporated after carbonation (oxidative condition), and then exsolved after DRM step (reductive condition).

Conventional carbonation and decarbonation studies (carbonation: 10 vol% CO_2/He at 700 °C for 15 min and decarbonation: 100 vol% He at 900 °C for 15 min) were conducted over $\text{Ca}_2\text{Ni}_{0.05}$ DFM and $\text{Ca}_2\text{Ni}_{0.05}\text{Ti}_{0.95}$ MFM to study NiO sintering caused by the stress-induced sintering of CaO/CaCO_3 (Figure S25, Supporting Information). As mentioned above, NiO of $\text{Ca}_2\text{Ni}_{0.05}$ DFM and $\text{Ca}_2\text{Ni}_{0.05}\text{Ti}_{0.95}$ MFM are supported on the CaO and the CaTiO_3 , respectively. The test over $\text{Ca}_2\text{Ni}_{0.02}\text{Ti}_{0.98}$ MFM was not conducted because Ni species exist as $\text{Ca}_{1+x}\text{Ni}_y\text{Ti}_{1-y}\text{O}_3$ phase without NiO phase in the as-prepared sample. CO_2 capture capacity of $\text{Ca}_2\text{Ni}_{0.05}$ DFM and $\text{Ca}_2\text{Ni}_{0.05}\text{Ti}_{0.95}$ MFM at the 1st cycle is 16.97 and 6.82 mmol CO_2/g , respectively, because $\text{Ca}_2\text{Ni}_{0.05}$ DFM contains more CaO contents than that of $\text{Ca}_2\text{Ni}_{0.05}\text{Ti}_{0.95}$ MFM. The CO_2 capture capacity of $\text{Ca}_2\text{Ni}_{0.05}$ DFM decreased gradually to 7.13 mmol CO_2/g at the 15th carbonation due to the morphological changes of the CaO/CaCO_3 after decarbonation. For $\text{Ca}_2\text{Ni}_{0.05}\text{Ti}_{0.95}$ MFM, CO_2 capture capacity slightly reduced from 6.82 to 4.56 mmol CO_2/g during 15 cycles of carbonation and decarbonation. The deactivation rate of CO_2 capture capacity during 15 cycles over $\text{Ca}_2\text{Ni}_{0.05}$ DFM was ≈ 5.4 -fold faster than that over $\text{Ca}_2\text{Ni}_{0.05}\text{Ti}_{0.95}$ MFM because CaTiO_3 addition between CaO grains suppressed the agglomeration from the volume expansion of CaO/CaCO_3 during CO_2 capture in $\text{Ca}_2\text{Ni}_{0.05}\text{Ti}_{0.95}$ MFM. The crystallite size of NiO and CaO before and after 15 cycles of carbonation/decarbonation were calculated using the Scherrer equation and are summarized in Table S5 (Supporting Information). The crystallite size of CaO in $\text{Ca}_2\text{Ni}_{0.05}$ DFM increased from 28.5 to 34.0 nm. The changes in surface morphology and porosity of $\text{Ca}_2\text{Ni}_{0.05}$ DFM from volume expansion of CaO/CaCO_3 structures, as well as relatively weak NiO-CaO interaction, could result in the aggregation of Ni species (15.9 to 38.2 nm) during the carbonation and decarbonation cycles. In contrast, the crystallite sizes of CaO and NiO of $\text{Ca}_2\text{Ni}_{0.05}\text{Ti}_{0.95}$ MFM are comparable before and after 15 cycles of carbonation/decarbonation (CaO: 24.3 to 26.0 nm, and NiO: 14.0 to 12.7 nm). The presence of CaTiO_3 in the intra-region of CaO grains could suppress the severe aggregation of CaO during carbonation and decarbonation cycles. In addition, NiO supported on CaTiO_3 instead

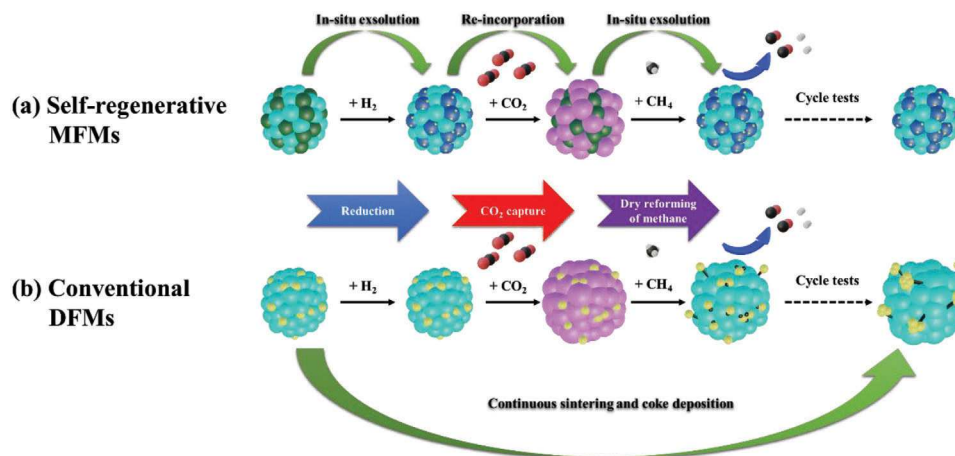


Figure 12. Schematics of ICCDRM over a) self-regenerative Ni-doped $\text{CaTiO}_3/\text{CaO}$ and b) conventional Ni/CaO DFM; dark green ($\text{Ca}_{1+x}\text{Ni}_y\text{Ti}_{1-x}\text{O}_3$), cyan (CaO), blue (CaTiO_3), yellow (Ni), purple (CaCO_3), black (coke).

of CaO/CaCO_3 decreases the occurrence of NiO mobility and sintering.

2.4. Mechanism of ICCDRM Over Self-Regenerative Ni-Doped $\text{CaTiO}_3/\text{CaO}$ MFM

Based on the physicochemical analysis and experimental results, a schematic of the mechanism over the self-regenerative Ni-doped $\text{CaTiO}_3/\text{CaO}$ ($\text{Ca}_2\text{Ni}_{0.02}\text{Ti}_{0.98}$) MFM and conventional Ni/CaO ($\text{Ca}_2\text{Ni}_{0.05}$) DFM in the ICCDRM process was illustrated (Figure 12). For conventional Ni/CaO DFM, NiO supported on CaO is reduced to Ni metal under the H_2 reduction step, $x\text{NiO}/\text{CaO}(\text{s}) + x\text{H}_2(\text{g}) \leftrightarrow x\text{Ni}^0/\text{CaO}(\text{s}) + x\text{H}_2\text{O}(\text{g})$. During the CO_2 capture step, the metallic Ni is oxidized by CO_2 (oxidative condition) to produce CO, and CaO captures CO_2 to produce CaCO_3 , $x\text{Ni}^0/\text{CaO}(\text{s}) + (x+1)\text{CO}_2(\text{g}) \leftrightarrow x\text{NiO}/\text{CaCO}_3(\text{s}) + x\text{CO}(\text{g})$. During the DRM step, NiO is reduced under CH_4 (reductive condition), and CO_2 desorbs from CaCO_3 and reacts with CH_4 to produce syngas (CO and H_2). In addition to DRM, CH_4 is decomposed to coke and H_2 , exacerbating the formation of filamentous coke growth between Ni and CaO. The overall reaction is as follows: $x\text{NiO}/\text{CaCO}_3(\text{s}) + (x+y+1)\text{CH}_4(\text{g}) \leftrightarrow y\text{C}-x\text{Ni}^0/\text{CaO}(\text{s}) + (x+2)\text{CO}(\text{g}) + 2(x+y+1)\text{H}_2(\text{g})$. The stress induced by the cyclical volume expansion and shrinkage from CaO to CaCO_3 (CaO: $16.9 \text{ cm}^3/\text{g}$ and CaCO_3 : $36.9 \text{ cm}^3 \text{ g}^{-1}$) during carbonation and decarbonation^[9] can contribute to rapid pore collapse of the structure. Additionally, the lower Tammann temperature of CaCO_3 (533°C) than the DRM operation temperature ($\approx 700^\circ\text{C}$) causes the loss of surface area, porosity, and sintering-induced decrease in CO_2 capture capacity.^[9,10] During each cycle, the reversible phase transformation of CaO to CaCO_3 weakens the Ni-CaO metal support interaction, resulting in significant sintering of Ni nanoparticles on the surface of CaO.^[11]

For the self-regenerative Ni-doped $\text{CaTiO}_3/\text{CaO}$ MFM, Ni nanoparticles are assembled and formed via exsolution from the $\text{Ca}_2\text{Ni}_{0.02}\text{Ti}_{0.98}$ perovskite lattice. The formed Ni nanoparticles are evenly distributed and partially submerged or socked in the CaTiO_3 perovskite oxide support and can be de-

scribed by the equation: $\text{Ca}_{1+x}\text{Ni}_y\text{Ti}_{1-y}\text{O}_{3-\delta}/(1-x)\text{CaO}(\text{s}) + \beta\text{H}_2(\text{g}) \leftrightarrow \alpha\text{Ni}^0/\text{Ca}_{1+x}\text{Ni}_y\text{Ti}_{1-y}\text{O}_{3-\delta}/(1-x)\text{CaO}(\text{s}) + \beta\text{H}_2\text{O}(\text{g})$. During the CO_2 capture step, exsolved Ni nanoparticles are re-incorporated into the subsurface of the CaTiO_3 lattice (e.g., self-regeneration) under CO_2 (oxidative condition), which is accompanied by CO production, and CaO reacts with CO_2 to produce CaCO_3 ; $\alpha\text{Ni}^0/\text{Ca}_{1+x}\text{Ni}_y\text{Ti}_{1-y}\text{O}_{3-\delta}/(1-x)\text{CaO}(\text{s}) + (\beta+1-x)\text{CO}_2(\text{g}) \leftrightarrow \text{Ca}_{1+x}\text{Ni}_y\text{Ti}_{1-y}\text{O}_{3-\delta}/(1-x)\text{CaCO}_3(\text{s}) + \beta\text{CO}(\text{g})$. Ni-doped $\text{CaTiO}_3/\text{CaO}$ MFMs exhibited stable CO_2 capture capacity during cyclic ICCDRM because CaTiO_3 acts as a physical barrier between CaO grains, suppressing the CaO sintering from CaO/ CaCO_3 volume expansion. During the subsequent DRM step, Ni nanoparticles exsolved from $\text{Ca}_2\text{Ni}_{0.02}\text{Ti}_{0.98}$ perovskite under CH_4 (reductive condition) and CO_2 desorbed from CaCO_3 reacts with CH_4 to produce syngas (CO and H_2), $\text{Ca}_{1+x}\text{Ni}_y\text{Ti}_{1-y}\text{O}_{3-\delta}/(1-x)\text{CaCO}_3(\text{s}) + (\beta+1-x)\text{CH}_4(\text{g}) \leftrightarrow \alpha\text{Ni}^0/\text{Ca}_{1+x}\text{Ni}_y\text{Ti}_{1-y}\text{O}_{3-\delta}/(1-x)\text{CaO}(\text{s}) + (\beta+2-2x)\text{CO}(\text{g}) + 2(\beta+1-x)\text{H}_2(\text{g})$. Moreover, Tammann temperatures of Ni and NiO are much higher (Ni: 863°C and NiO: 1114°C) than the typical DRM operation temperature (700°C).^[10] This means the Ni sintering in the $\text{Ca}_2\text{Ni}_{0.05}$ DFM is predominately caused by the volume expansion (CaO to CaCO_3) and weak interaction between Ni and CaO during the cyclic ICCDRM. Therefore, the separation of Ni species socked in CaTiO_3 from CaO grains prevents significant Ni sintering and prolongs ICCDRM activity.

3. Conclusions

In this paper, Ni-doped $\text{CaTiO}_3/\text{CaO}$ nanocomposite ($\text{Ca}_2\text{Ni}_{0.02}\text{Ti}_{0.98}$) as MFMs was prepared for ICCDRM. A small amount of Ni can be incorporated into CaTiO_3 perovskite as a $\text{Ca}_{1+x}\text{Ni}_y\text{Ti}_{1-y}\text{O}_3$ perovskite because of an unstable NiO_6 octahedron. In-situ exsolved Ni nanoparticles, which interact strongly with the CaTiO_3 perovskite oxide support, were evenly distributed on the surface after reductive conditions (H_2 or CH_4). The Ni nanoparticles exsolved in CaTiO_3 migrate back to the subsurface during CO_2 capture (oxidative conditions), resulting in self-regeneration. In addition, in-situ exsolved Ni nanoparticles, which interact strongly with host CaTiO_3

perovskite, exhibited excellent resistance to filamentous coke deposition under CH_4 conditions. Some deposited coke was in situ gasified by surface lattice oxygen of CaTiO_3 perovskite. The Ni-doped $\text{CaTiO}_3/\text{CaO}$ MFM showed relatively stable CO_2 capture capacity and syngas productivity during 30 cycles of IC-CDRM. The presence of CaTiO_3 between CaO grains prevented volume expansion, maintaining the CO_2 capture capacity. The strong interaction between Ni and CaTiO_3 , separation from CaO/CaCO_3 morphology change, and self-regeneration during CO_2 capture and subsequent DRM (redox condition) can mitigate Ni sintering. Due to the small size of exsolved Ni particles and their strong interaction with CaTiO_3 , there was no severe coke build-up. Additionally, coke gasification occurred by lattice oxygen during the CO_2 capture process. Therefore, our results show that Ni-doped $\text{CaTiO}_3/\text{CaO}$ MFM can potentially overcome current challenges for the ICCDRM process. Future efforts will optimize the self-regenerative MFMs for improved ICCDRM performance and multicycle stability.

4. Experimental Section

Preparation of MFMs: The $\text{Ca}_x\text{Ni}_y\text{Ti}_{1-y}$ ($x = 1$, and 2, and $y = 0$, 0.01, 0.02, and 0.05) perovskite materials were prepared using the sol-gel Pechini method. $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Alfa Aesar), $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (Sigma-Aldrich), and $\text{Ti}(\text{C}_4\text{H}_9\text{O})_4$ (Arcros Organics) were used for the Ni, Ca and Ti precursors, respectively. Citric acid (Alfa Aesar) and ethylene glycol butyl ether (Sigma-Aldrich) were used as chelating and polymerization agents. The required amounts of metal precursors were mixed in a stoichiometric ratio and dissolved in DI water to form an aqueous solution. Citric acid (the molar ratio of citric acid to metal ions was 1) and ethylene glycol butyl ether (the molar ratio of citric acid to ethylene glycol butyl ether was 3) were added into the precursor solution. The solution was dried in an oven overnight at 120°C to form a dried gel. The resulting gel was ground finely with mortar and pestle and calcined in a muffle furnace at 800°C for 5 h with a temperature ramp rate of 5°C min^{-1} .

using a $\text{Cu K}\alpha$ radiation source. The crystallite sizes of CaO and NiO were calculated using the Scherrer equation. The chemical composition of the surface of MFMs was obtained in an XPS using an Axis Ultra spectrometer (Kratos Analytical) equipped with an Al $\text{K}\alpha$ source. The atomic resolution images and crystalline phase of the MFMs were obtained by STEM-HAADF and HRTEM using a ThermoFischer Scientific Titan Themis 300 with double spherical aberration-correctors operated at 300 kV. TPR was used to investigate the reducibility of the MFMs (50 mg) under 5% H_2/He (H_2 -TPR) or 10% CH_4/He (CH_4 -TPR) with total flow rate of 50 ml min^{-1} from 100 to 800°C with temperature ramping of $10^\circ\text{C min}^{-1}$ after pretreatment in 20% O_2/He condition at 800°C for 1 h in a quartz tube microreactor (Hidden Analytical CATLAB) combined with a MS spectrometer (Hidden QGA Gas Analyzer). TPO was conducted under 20 vol% O_2/He from 100 to 800°C with a temperature ramping rate of $10^\circ\text{C min}^{-1}$ in a quartz tube microreactor (Hidden Analytical CATLAB) and MS spectrometer (Hidden QGA Gas Analyzer) to determine the type of coke species after CH_4 -treatment under 10 vol% CH_4/He with total flow rate of 50 ml min^{-1} at 800°C for 1 h over MFMs.

Reaction Process: The CO_2 capture and subsequent DRM was conducted using 50 mg of MFMs in a quartz tube microreactor (Hidden Analytical CATLAB) combined with an MS spectrometer (Hidden QGA Gas Analyzer) after reduction under 5% H_2/He condition at 800°C for 1 h. The temperature was decreased to 600, 650, and 700°C , which was maintained during the reaction. At the CO_2 capture step, 10 vol% CO_2/He flowed through the bed with 50 ml min^{-1} total flow rate for 15 min. At the subsequent DRM step, the gas composition changed to 10 vol% CH_4 and was maintained for 15 min.

Conventional carbonation and decarbonation was carried out using 50 mg of MFMs in a quartz tube microreactor (Hidden Analytical CATLAB) combined with an MS spectrometer (Hidden QGA Gas Analyzer) after pretreatment in 20% O_2/He condition at 800°C for 1 h. At the CO_2 capture step, 10 vol% CO_2/He flowed through the bed with 50 ml min^{-1} of total flow rate at 700°C for 15 min. At the regeneration step, the temperature increased to 900°C with temperature ramping of $10^\circ\text{C min}^{-1}$ and maintained under pure He for 15 min.

CO_2 capture capacity during CO_2 capture step, syngas (CO and H_2) productivity during DRM step and H_2/CO ratio were calculated following equations (3)–(5):

$$\text{CO}_2 \text{ capture capacity (mmol/g) during CO}_2 \text{ capture} = \frac{\int \left\{ \text{Inlet CO}_2 \text{ molar flow rate} \left(\frac{\text{mmol}}{\text{min}} \right) - \text{Outlet CO}_2 \text{ molar flow rate} \left(\frac{\text{mmol}}{\text{min}} \right) \right\} dt}{\text{Weight of sample (g)}} \quad (3)$$

$$\text{Syngas (CO and H}_2\text{) productivity (mmol/g) during DRM} = \frac{\int \text{Produced syngas (CO or H}_2\text{) molar flow rate} \left(\frac{\text{mmol}}{\text{min}} \right) dt}{\text{Weight of sample (g)}} \quad (4)$$

Perovskite Structure Factors: The perovskite structure factors were calculated to predict the stability of the perovskite oxide structure. The Goldschmidt tolerance factor, t , of perovskite (ABO_3), is defined as follows:

$$t = \frac{r_A + r_O}{\sqrt{2} (r_B + r_O)} \quad (1)$$

Octahedron factor, μ , related to octahedral unit BO_6 , is defined as follows:

$$\mu = \frac{r_B}{r_O} \quad (2)$$

where r_A and r_B are the ionic radius of the A and B cations, respectively, and r_O is the ionic radius of the O anion.

Materials Characterization: The crystallographic structure of the MFMs was characterized by XRD analysis (PANalytical Empyrean Series 2)

$$\text{H}_2/\text{CO ratio} = \text{H}_2 \text{ productivity} / \text{CO productivity} \quad (5)$$

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

dry reforming of methane, integrated CO₂ capture and utilization, multi-functional materials, nickel doped-calcium titanates, self-regeneration

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