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ARTICLE

Integrated SO_2/NO_2-containing CO_2 capture and methane dry reforming over Ni-Ca dual functional material: A mechanistic study

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Bocheng Yu,[a] Muqing Yang,[a] Yijian Qiao,[a] Yaozu Wang,[a] Yongqing Xu,[a] Xuan Bie,[a] Qinghai Li,[a] Yanguo Zhang,[a] Shuzhuang Sun*[b] and Hui Zhou*[ac]

Integrated carbon capture and utilization (ICCU) has emerged as a promising strategy toward carbon neutrality. However, most existing studies rely on simulated flue gas compositions, neglecting the impact of common impurities such as sulfur oxides (SOx) and nitrogen oxides (NOx), thereby limiting the practical industrial applicability of ICCU technologies. Herein, we systematically investigate the effects of SO_2 and NO_2 at various concentrations on the adsorption-catalysis performance based on a representative Ni-Ca dual functional material (DFM) in ICCU-dry reforming of methane (ICCU-DRM) process. Exposure to 100 ppm SO_2 showed negligible influence on catalytic activity but markedly inhibited carbon deposition. Further increasing the SO_2 concentration to 500 ppm led to complete deactivation of the DFM. NO_2 exhibited a similar concentration-dependent trend to SO_2, albeit with a comparatively lower impact. Mechanistic analysis revealed that both SO_2 and NO_2 promote the formation of a coating layer of calcium-containing compounds on the surface of Ni nanoparticles, accounting for the part or total deactivation. These findings offer critical insights into the industrial applications of ICCU systems under realistic flue gas conditions.

Keywords: Integrated carbon capture and utilization; SOx and NOx; Deactivation; Phase transition; DRM.

1. Introduction

Excessive anthropogenic CO_2 emissions are causing severe global warming, leading to the frequent occurrence of extreme weather.[1,2] Carbon capture, utilization and storage (CCUS) are believed as one of the most promising ways to achieve net zero by this mid-century as an industrial-level technology.[3–5] Compared to carbon capture and storage (CCS), carbon capture and utilization (CCU) can convert the captured CO_2 into high-value chemical products (CO, CH_4, CH_3OH, etc.), which shows a better economy with the avoidance of carbon leaks. Among most of the C1 production reactions (reverse water gas shift, methanation, etc.), dry reforming of methane (DRM, Eq. 1) can simultaneously convert two main greenhouse gases CH_4 and CO_2 into syngas, which serves as a feedstock for other important chemical reactions like methanol production and Fischer-Tropsch synthesis.[6,7] However, high CO_2 storage and transportation costs and massive energy consumption on temperature and pressure swing operations severely restrain the wide deployment of CCU technologies.[8,9]

$$CO_2+CH_4 \rightarrow 2CO+2H_2 \quad \Delta H = +274 \text{ kJ mol}^{-1} \qquad \text{(Eq. 1)}$$

Recently, by combining the CO_2 capture and chemical utilization into one reactor, integrated carbon capture and utilization (ICCU) has gained increasing interest from researchers and engineers.[10–14] To achieve these two processes in one reactor, dual function materials (DFMs), consisting of adsorptive component for carbon capture and catalytic component for carbon

[a] Key Laboratory for Thermal Science and Power Engineering of Ministry of Education, Beijing Key Laboratory of CO2 Utilization and Reduction Technology, Department of Energy and Power Engineering, Tsinghua University, Beijing 100084, P.R. China.
[b] School of Chemical Engineering, Zhengzhou University, Zhengzhou 450001, P.R. China.
[c] 3Shanxi Research Institute for Clean Energy, Tsinghua University, Taiyuan, Shanxi 030000, P.R. China
[d] * Corresponding authors. Emails: ssun@zzu.edu.cn; huizhou@tsinghua.edu.cn.

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conversion, are crucial to achieve high performance ICCU process.[15–18] Since DRM is a strongly endothermic reaction and needs high temperature condition (600–900°C), Ca-based sorbents are the most promising candidates for carbon capture.[19,20] However, Ca-based sorbents severely suffer from sintering, leading to a sharp decreased CO_2 capacity after cycles.[21,22] Thus, promoters including MgO, Al_2O_3 and ZrO_2 are commonly introduced into the DFMs to enhance the CaO stability by acting as the physical barrier.[23–25] Ni as an earth-abundant metal, showing excellent catalytic activity to methane activation, has become one of the most impressive choices for the catalytic components.[26–28]

Previous studies focused on the outperformed DFM design and adsorptive-catalytic mechanism investigation via ideal flue gas (a mixture of CO_2 and N_2), while few studies investigate the influence of impurity components in the realistic flue gas. SO_x and NO_x, as two of the most important pollutions in flue gas, have been proven to significantly influence the capture and conversion performance.[29–31] Previous studies reported that SO_2 and NO_2 could poison the CO_2 hydrogenation catalysts, primarily attributed to the strong chemisorption of intermediate species on active metal sites or generation of stable metal sulfides which irreversibly block active sites.[32,33] Also, as an alkaline sorbent, CaO can adsorb acidic SO_2 and NO_2, affecting its adsorptive performance.[34,35] Notably, as for the ICCU-DRM process, the reaction atmosphere frequently switches between oxidizing atmosphere (CO_2/N_2) and reductive atmosphere (CH_4/N_2), which brings new understandings compared to independent capture or conversion scenarios.

Herein, we investigated the influence of SO_2 and NO_2 on typical Ni-Ca DFMs. Ni5Al15Ca DFM as a representative DFM for ICCU-DRM was synthesized by the sol-gel methods, in which Ni provides high catalytic activity, CaO captures CO_2 in flue gas and Al_2O_3 acts as stabilizer. Series tests under different SO_2 and NO_2 concentrations were performed to uncover the influence of the pollution in flue gas. Low concentration of SO_2 (100 ppm) containing in flue gas showed negligible influence on catalytic activity but markedly reduced H_2:CO ratio. Further increasing the SO_2 concentration to 500 ppm resulted in complete deactivation of the DFM. NO_2 showed a similar phenomenon to SO_2 with a comparatively lower impact. Systematic characteristics were performed and revealed that the formation of a coating layer on the surface of Ni nanoparticles induced by SO_2 and NO_2, accounting for the part or total deactivation. This study aims to offer critical insights into the industrial applications of ICCU systems under realistic flue gas conditions.

2. Results and discussion

2.1 Performance evaluation of SO_2 and NO_2 influence

The impact of SO_2 and NO_2 in flue gas on the performance of ICCU-DRM was evaluated through a series of tests under varying SO_2 and NO_2 concentrations (100, 200, and 500 ppm). Without SO_2 or NO_2 in flue gas, the performance of the Ni5Al15Ca DFM was first assessed in the absence of SO_2 and NO_2. The real-time concentrations of CO_2, CO, H_2, and CH_4 during the first and second cycles are shown in Fig. 1. During the CO_2 capture stage, CO_2 was adsorbed by CaO, accompanied by CO formation attributed to the reverse Boudouard reaction ($CO_2+C \rightarrow 2CO$) from the second cycle. The elevated CO amount indicate the severe carbon deposition during the previous dry reforming stage. In the subsequent dry reforming stage, CH_4 reacted with the captured CO_2 to produce CO and H_2. Simultaneously, CH_4 could decompose into carbon and H_2 as a common side reaction. Notably, although CO was no longer detected at the final of dry reforming stage, H_2 remained generated, highlighting the strong CH_4 decomposition activity of Ni sites.

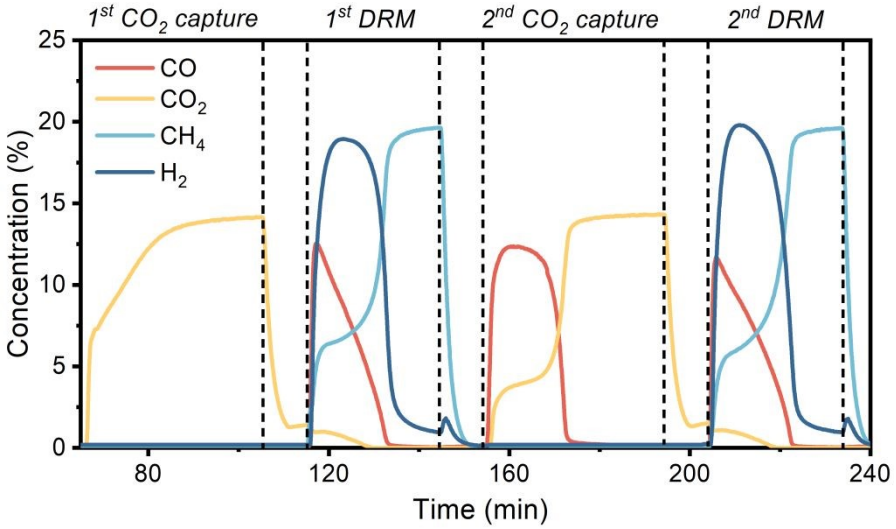

Fig. 1 Real-time gas concentrations of ICCU-DRM for the first and second cycle.

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The cyclic performance of the Ni5Al15Ca DFM was systematically evaluated, as illustrated in Fig. 2. CO_2 conversion as a primary indicator of catalytic efficiency reached 81.3% in the first cycle and exhibited only a slight decline to 76.3% after 10 cycles (Fig. 2a). Result confirms the high activity and stability of the Ni active sites to dry reforming process. Despite the CO_2 conversion, the H_2:CO ratio was notably higher than the ideal stoichiometric value of 1, reaching 2.39 in the first cycle (Fig. 2b). This deviation suggests the occurrence of CH_4 decomposition as a side reaction, which contributes to excess hydrogen production and promotes carbon deposition on the catalyst surface. The elevated carbon accumulation was further evidenced by the CO yield during the carbonation stage (Fig. 2d). Notably, the CO_2 capacity of Ni5Al15Ca remained relatively stable over the 10 cycles, only decreasing from 10.9 to 9.5 mmol g^{-1} (Fig. 2c). Such stability is attributed to the presence of Al_2O_3, which can act as a physical barrier during cycles.

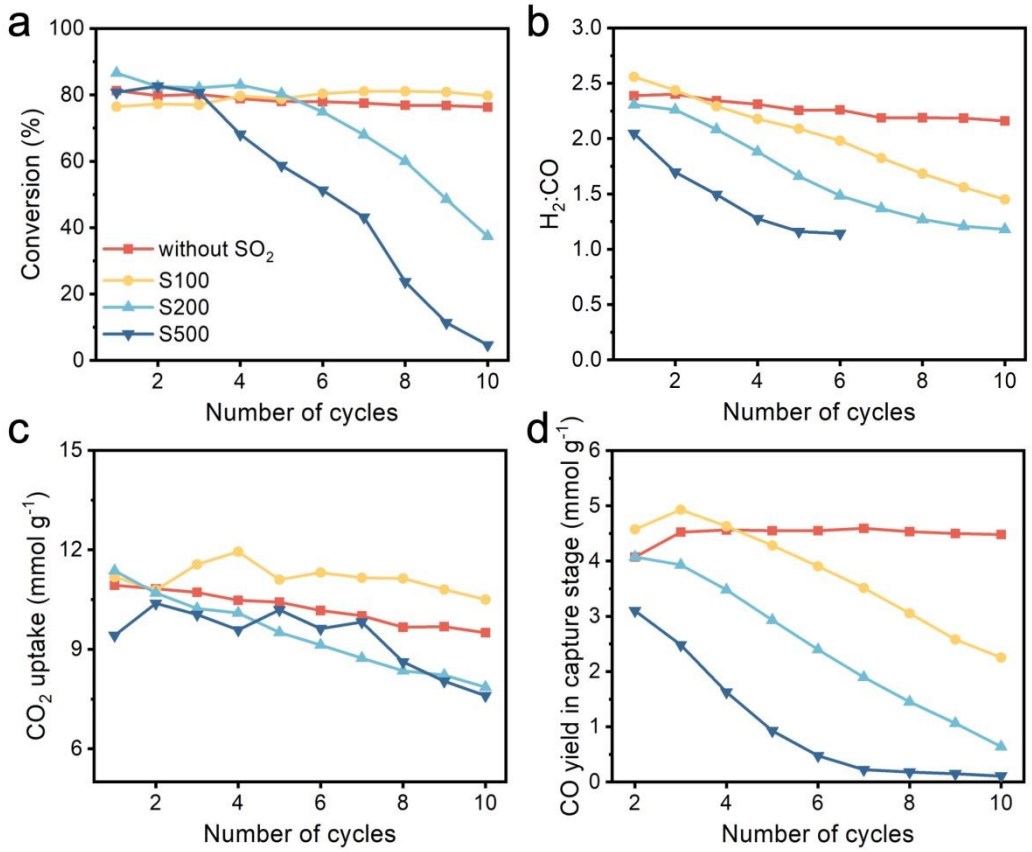

Fig. 2 Cyclic performance of ICCU-DRM under SO_2-containing flue gas.
(a) CO_2 conversion, (b) H_2:CO ratio, (c) CO_2 uptake and (d) CO yield in capture stage. S100 refers to the cycled DFM with 100 ppm SO_2 in flue gas.

The influence of varying SO_2 concentrations (100, 200, and 500 ppm) on the performance of the Ni5Al15Ca DFM was investigated. As shown in Fig. 2a, under 100 ppm SO_2 condition, the DFM reached CO_2 conversion of 79.4% in the 10th cycles, even slightly higher than the SO_2-free DFM. However, as for 200 ppm SO_2, a significant decline in CO_2 conversion was observed over cycles, with CO_2 conversion dropping to just 37.4% for the 10th cycle. Further increasing the SO_2 concentration to 500 ppm resulted in severe deactivation, with CO and H_2 becoming undetectable in the 10th cycle. Results demonstrate that low SO_2 concentration show negligible impact on the CO_2 conversion performance, while higher concentrations lead to significant DFM deactivation for ICCU-DRM.

The H_2:CO ratio as another key performance indicator was also examined, as presented in Fig. 2b. Interestingly, under 100 ppm SO_2, the H_2:CO ratio gradually decreased over cycles and approached the ideal stoichiometric value of 1, and a similar but more significant trend can be observed at 200 ppm SO_2. Results suggest that SO_2 in flue gas can suppress the CH_4 decomposition side reaction, thereby mitigating carbon deposition. Decreasing carbon deposit could further be supported by the decreased CO yield during the subsequent carbonation stage (Fig. 2d). Since both CO and H_2 production diminished to near-zero levels after the 6th cycle under 500 ppm SO_2, the H_2:CO ratio was irrelevant in the final 4 cycles. Notably, the absence of CO during the carbonation stage under 500 ppm SO_2 condition also suggested that no carbon deposition occurred.

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Collectively, these findings indicate that SO_2 can reduce carbon deposition and improve product selectivity for dry reforming process.

The observed differences in CO_2 conversion and H_2:CO ratio between SO_2-containing and SO_2-free conditions can be attributed to different reaction kinetics. Thus, the real-time gas concentrations for the 1st and 10th cycles are presented in Fig. 3. For the Ni5Al15Ca DFM under SO_2-free condition, negligible differences were observed between the 1st and 10th cycles, suggesting that the Ni active sites remained catalytically stable for both methane dry reforming and methane decomposition. However, after introducing low concentrations of SO_2 to DFM, a rapid catalytic activity loss was observed, evidenced by the slower formation of both CO and H_2. SO_2 exhibited a more pronounced inhibitory effect on CH_4 decomposition than on the dry reforming reaction, resulting in relatively unchanged CO_2 conversion but a significantly decreased H_2:CO ratio. This shift indicates a suppression of the side reaction responsible for excess methane consumption and carbon deposition. At higher SO_2 concentrations, however, the CO_2 conversion itself became adversely affected, resulting in nearly complete deactivation.

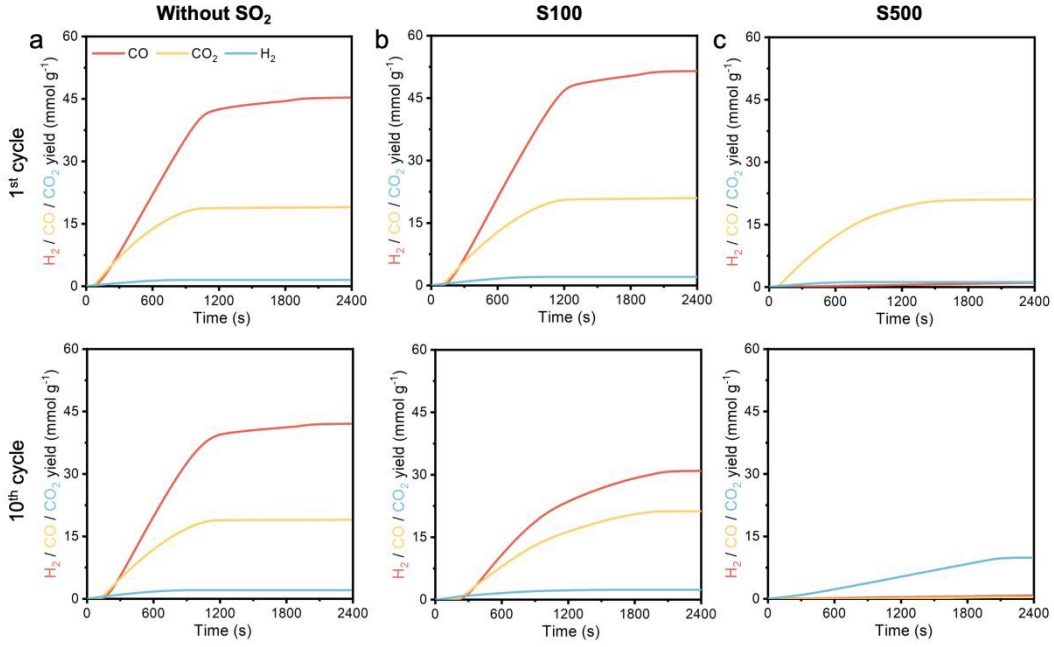

Fig. 3 Real-time gas concentration with SO_2-containing flue gas of ICCU-DRM for the 1st and 10th cycles.
(a) without SO_2 or NO_2 in flue gas, (b) 100 ppm SO_2-containing flue gas, and (c) 500 ppm SO_2-containing flue gas.

Furthermore, the effect of SO_2 on the cyclic stability of CO_2 capture by the Ni5Al15Ca DFM was assessed, as shown in Fig. 2c. Under 100 ppm SO_2, the initial CO_2 uptake was comparable to the SO_2-free conditon. Notably, Ni5Al15Ca even exhibited an improved capacity retention under such condition, with only 6.1% decrease after 10 cycles, compared to 13.6% decrease observed in the DFM without SO_2 or NO_2. Enhanced stability could be attributed to the formation of thermally stable species such as CaS and $CaSO_4$ (vide infra), which could act as physical barriers to suppress the CaO sintering. However, increasing SO_2 concentrations led to declined CO_2 uptake with cycling. Such deactivation was likely due to the continuous formation of CaS and $CaSO_4$, consuming active CaO components and thereby reducing the theoretical CO_2 capacity of the DFM. In short, while limited formation of these sulfur-containing phases may enhance stability by serving as physical barriers, excessive accumulation compromises the sorbent capacity until equilibrium is reached.

The influence of NO_2 in the flue gas was further investigated, as shown in Fig. 4. Similar to SO_2, NO_2 induced a similar CO_2 conversion but a shift in the H_2:CO ratio; however, its impact was significantly less severe. Notably, the Ni5Al15Ca DFM retained considerable catalytic activity even under 500 ppm NO_2, whereas complete deactivation occurred under the same concentration of SO_2. These differences can be attributed to the relatively milder deactivation of Ni active sites by NO_2, as compared to SO_2, for both dry reforming and methane decomposition reactions (Fig. 5). In addition, NO_2 had minimal effect on CO_2 uptake capacity, likely because nitrogen species do not accumulate within the DFM (vide supra). Overall, while NO_2 exhibits a similar mode of influence to SO_2, its detrimental effects are significantly less pronounced.

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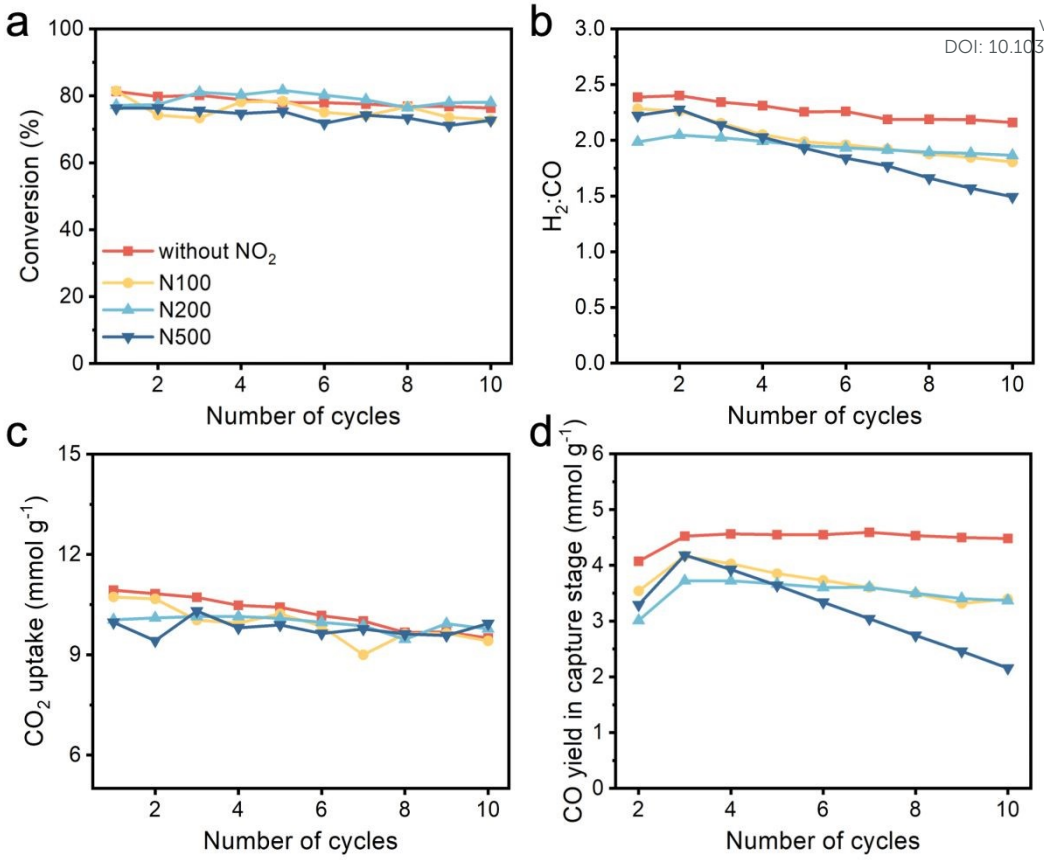

Fig. 4 Cyclic performance of ICCU-DRM under NO_2-containing flue gas.

(a) CO_2 conversion, (b) H_2:CO ratio, (c) CO_2 uptake and (d) CO yield in capture stage. N100 refers to the cycled DFM with 100 ppm NO_2 in flue gas.

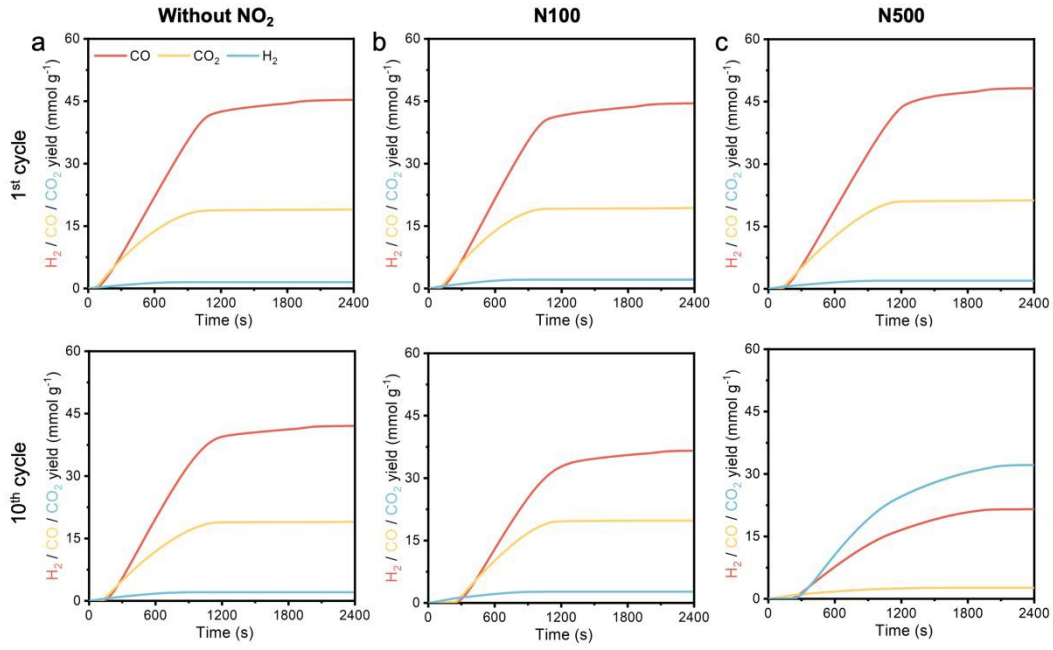

Fig. 5 Real-time gas concentration with NO_2-containing flue gas of ICCU-DRM for the 1st and 10th cycles.

(a) without SO_2 or NO_2 in flue gas, (b) 100 ppm NO_2-containing flue gas, and (c) 500 ppm NO_2-containing flue gas.

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2.2 Mechanism study of the SO_2 and NO_2 influences

To elucidate the performance impacts of SO_2 and NO_2, a series of systematic characterizations were conducted to reveal the underlying mechanisms. The elemental composition of the as-synthesized Ni5Al15Ca material, determined by inductively coupled plasma optical emission spectroscopy (ICP-OES), is summarized in Table 1. X-ray diffraction (XRD) (Fig. 6a) indicated that the pre-reduced Ni5Al15Ca was primarily composed of CaO (PDF# 96-900-8606) and metallic Ni (PDF# 96-151-2527), while Al existed in an amorphous phase. Scanning electron microscopy (SEM) revealed that the pre-reduced Ni5Al15Ca DFM possessed a porous morphology (Fig. 6b), and transmission electron microscope (TEM) further confirmed the dispersion of Ni nanoparticles on the blocky CaO support (Fig. 6c). N_2 physisorption measurements (Fig. 6d) showed a specific surface area of 13.4 m^2 g^{-1} with an average pore diameter of 23.6 nm, indicative of a mesoporous structure of DFM. H_2 temperature-programmed reduction (H_2-TPR) analysis (Fig. 6e) demonstrated the reducibility of NiO or Ni–Al spinel species to metallic Ni under H_2, which was consistent with the XRD and TEM observations. The CO_2 uptake capacity of the pre-reduced DFM was measured to be 10.4 mmol g^{-1} by thermal gravimetric analyzer (TGA), in good agreement with the results obtained from the fixed-bed reactor experiments (Fig. 6f).

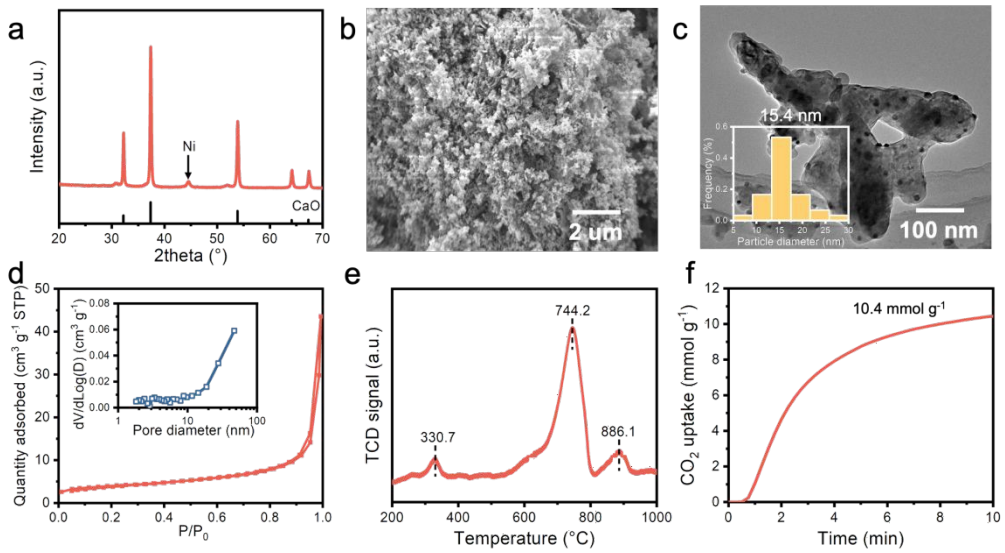

Fig. 6 Characteristics of pre-reduced Ni5Al15Ca dual functional material.

(a) XRD of pre-reduced DFM, (b) SEM of pre-reduced DFM, (c) TEM of pre-reduced DFM, (d) surface area and pore diameter distribution of the pre-reduced DFM, (e) H_2-TPR of calcined DFM and (f) TGA of pre-reduced DFM.

Table 1. Elementary analysis of pre-reduced and cycled DFM.

DFM	Ni [a] (%)	Al (%)	Ca (%)	S (%)
Pre-reduced	5.1	6.6	57.1	-
Cycled-S100	4.2	6.0	45.6	1.6
Cycled-S500	4.1	5.8	44.5	5.9

[a] Mass ratio of Ni, Al, Ca and S was tested by ICP-OES

The crystal structures of cycled Ni5Al15Ca DFMs were analyzed by XRD, as shown in Fig. 7. After 10 cycles under SO_2- and NO_2-free conditions, the characteristic phases of CaO and metallic Ni remained detectable, although the significant decrease in peak intensity was attributed to the formation of amorphous carbon deposits. When cycled in flue gas containing SO_2, new diffraction peaks corresponding to CaS (PDF# 96-900-8607) appeared at both 100 ppm and 500 ppm SO_2 concentrations, whereas a minor $CaSO_4$ (PDF# 96-900-4097) phase was only observed at 500 ppm SO_2. The accumulation of sulfur species after 10 cycles in SO_2-containing atmospheres was further confirmed by ICP-OES. Given the relative stability of $CaSO_4$ and CaS under dry reforming conditions, the sulfur content reached approximately 1.6% and 5.9% for the 100 ppm and 500 ppm SO_2 cases, respectively (Table 1). However, for the samples exposed to NO_2-containing flue gas, only CaO and Ni phases were detected by XRD. Notably, higher NO_2 concentrations corresponded to increased peak intensities, consistent with the suppression of carbon deposition (vide supra). Elemental analysis showed no detectable nitrogen in the cycled DFM, indicating that nitrogen species did not accumulate during methane dry reforming.

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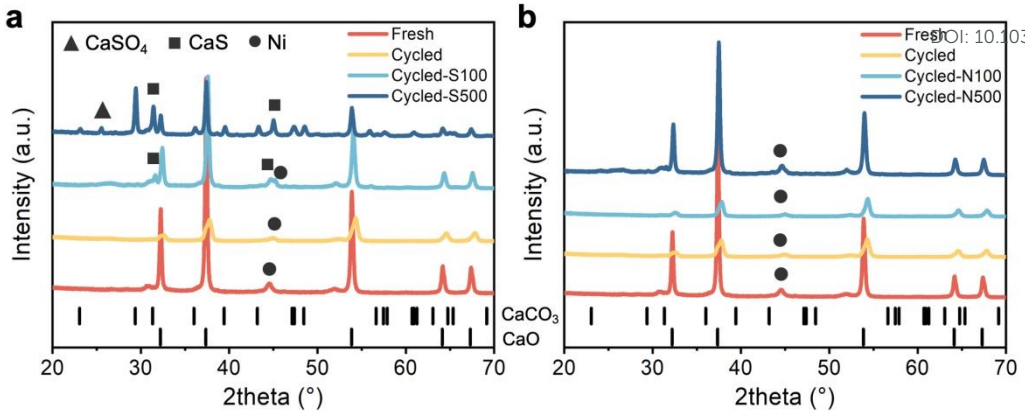

Fig. 7 XRD of pre-reduced and cycled DFMs.

(a) SO_2-containing and (b) NO_2-containing flue gas.

Given the significant impact of SO_2 on the crystal phase changing of the DFM, in situ XRD was conducted to elucidate the dynamic phase transformations during the carbonation and dry reforming stages (Fig. 8). Upon introduction of SO_2-containing flue gas into the reactor, the characteristic CaO peaks gradually diminished concurrent with the emergence of $CaCO_3$ peaks (PDF# 96-900-0967), confirming effective CO_2 capture. Notably, $CaSO_4$ was detected at the onset of the carbonation stage, reflecting the adsorption of SO_2 by the CaO sorbent. As the reaction progressed, CaS formation could be observed, likely resulting from the disproportionation of SO_2 (Eq. 2). During the conversion stage, in addition to the decomposition of $CaCO_3$ regenerating CaO, an increase in CaS peak intensity accompanied by a decrease in $CaSO_4$ peak intensity was detected. This trend is consistent with the reduction of $CaSO_4$ by CH_4 to form CaS (Eq. 3) [36].

$$4CaO+4SO_2 \rightarrow 3CaSO_4+CaS \quad \Delta H = -1059 \text{ kJ mol}^{-1} \qquad \text{Eq. (2)}$$

$$CH_4+CaSO_4 \rightarrow CO_2+CaS+2H_2O \quad \Delta H = +162 \text{ kJ mol}^{-1} \qquad \text{Eq. (3)}$$

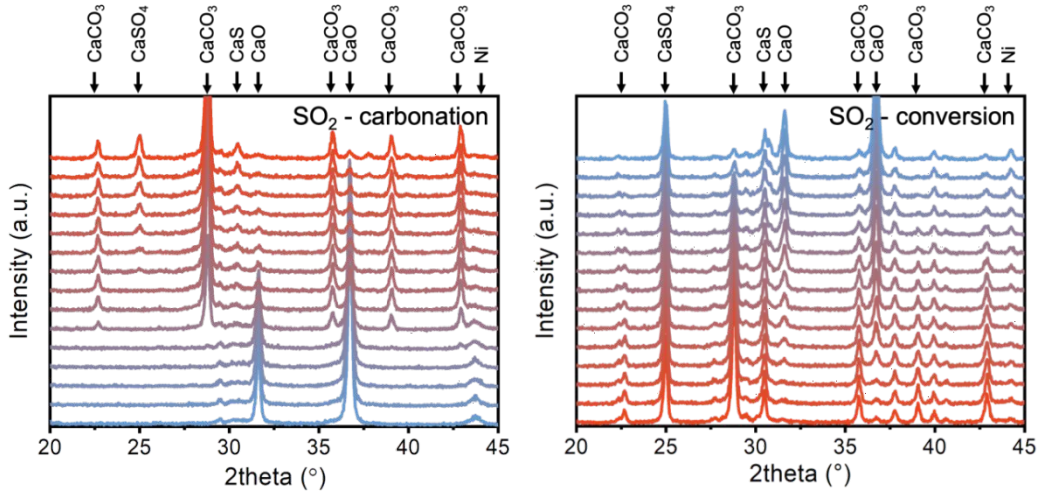

Fig. 8 In situ XRD of ICCU-DRM under SO_2-containing flue gas.

Each scan continued for 2.5 min.

The surface morphologies of the cycled DFMs are shown in Fig. 9. Severe pore collapse was observed after cycling, suggesting that the Ni5Al15Ca DFM underwent significant sintering. Notably, no discernible morphological differences could be observed between DFMs cycled in SO_2- or NO_2-containing atmospheres to without SO_2 or NO_2 condition, indicating that SO_2 and NO_2 had minimal influence on surface morphology. However, both SO_2 and NO_2 exhibited clear effects on the pore structure, as evidenced by N_2 physisorption analysis (Fig. 10 and Table 2). Compared with the pre-reduced DFM, most cycled samples, except for the DFM exposed to 500 ppm SO_2, exhibited an increase in surface area, primarily due to carbon deposition. Prior studies have shown that sintering of CaO-based DFMs typically results in a decreased pore diameter due to the collapse of macropores. In the presence of SO_2, the average pore diameter increased to 24.2 nm and 33.0 nm (at 100 ppm and 200 ppm, respectively), in contrast to the 16.8 nm observed in the SO_2-free cycled DFM. Increased pore diameter

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was likely due to the formation of CaS and $CaSO_4$, as confirmed by XRD. Sulfur-containing species was ascribed to the increased Tammann temperatures, which function as physical barriers to effectively suppress CaO sintering. Interestingly, a similar trend could be observed in the NO_2-containing case, despite the absence of stable nitrogen-containing crystal phases. The increase in pore diameter for NO_2-treated DMF was hypothesized to result from pore generation during the decomposition of transient calcium nitrite intermediates.

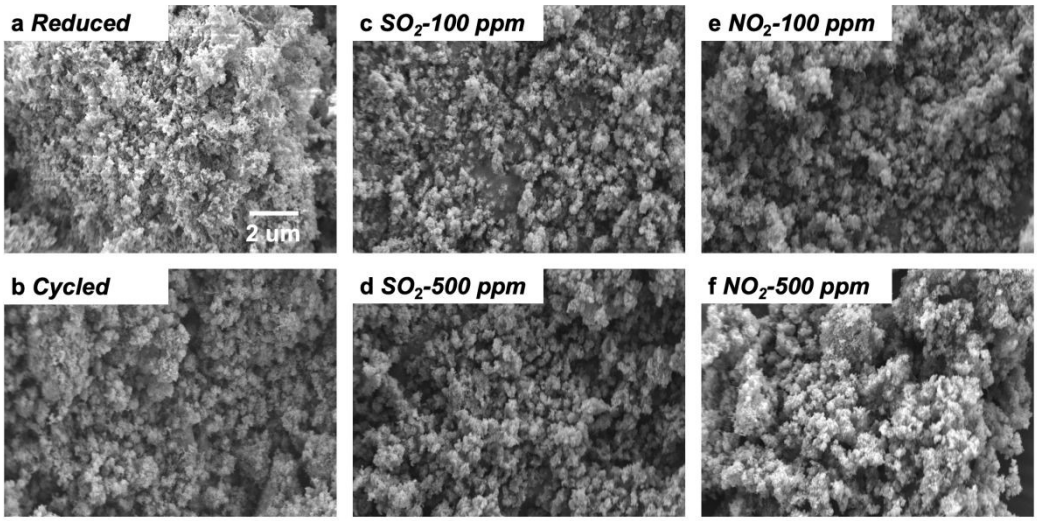

Fig. 9 SEM of pre-reduced and cycled Ni5Al15Ca DFM.

(a) Pre-reduced DFM, (b) cycled DFM without SO_2 or NO_2, (c) cycled DFM with 100 ppm SO_2-containing flue gas, (d) cycled DFM with 500 ppm SO_2-containing flue gas, (e) cycled DFM with 100 ppm NO_2-containing flue gas, and (f) cycled DFM with 500 ppm NO_2-containing flue gas.

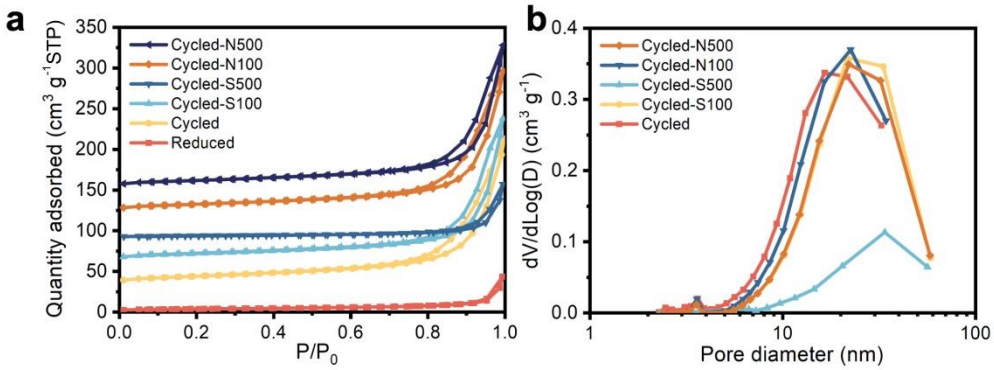

Fig. 10 N_2 physisorption of cycled DFM.

(a) BET surface and (b) pore diameter distribution.

Table 2. BET surface and averaged pore diameter of pre-reduced and cycled DFM.

DFM	BET surface (m^2 g^{-1})	Averaged pore diameter[a] (nm)
Pre-reduced	13.4	23.6
Cycled	49.6	16.8
Cycled-S100	42.0	24.2
Cycled-S500	13.0	33.0
Cycled-N100	44.5	18.9
Cycled-N500	41.8	24.2

[a]The pore diameter was calculated by BJH desorption branch (4V/A).

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The Ni nanoparticles and elemental distribution were further examined by TEM equipped with energy-dispersive X-ray analysis (EDX), as shown in Fig. 11. Pre-reduced and cycled DFM exhibited similar Ni nanoparticle size, indicated that sintering played a minor role in deactivation of Ni active sites. After 10 cycles without SO_2 or NO_2, carbon nanotubes (CNTs) were observed, originating from carbon deposition during CH_4 decomposition. Under 100 ppm SO_2, the morphology of Ni nanoparticles remained unchanged, indicating that low-concentration SO_2 exhibited minimal influence on the nano structure. However, at elevated SO_2 concentrations (500 ppm), CNTs were no longer observed, which was consistent with the reduced carbon deposition observed in fixed-bed reactor tests. Line-scan EDX analysis revealed a strong spatial correlation between sulfur and nickel signals (Fig. 11c), even though no NiS phases were detected by XRD. Close-up lattice-resolved imaging further confirmed the presence of NiS by identifying lattice fringes with a spacing of 0.322 nm, corresponding to the (111) crystal plane of NiS. the. These results suggest that sulfur, likely in the form of CaS or NiS, coated the surface of Ni nanoparticles, leading to blockage of active sites and consequent catalytic deactivation. In the case of NO_2-containing flue gas, similar nanoparticle morphology was observed, while N element was undetectable in the EDX, in agreement with bulk elemental analysis. Although NO_2 did not leave a residual nitrogen species on the DFM after cycling, TEM images (Fig. 11e) revealed a distinct coating layer of CaO. This could be attributed to the acidic nature of NO_2, which likely promote surface restructuring of the alkaline CaO, resulting in the formation of a coating layer.

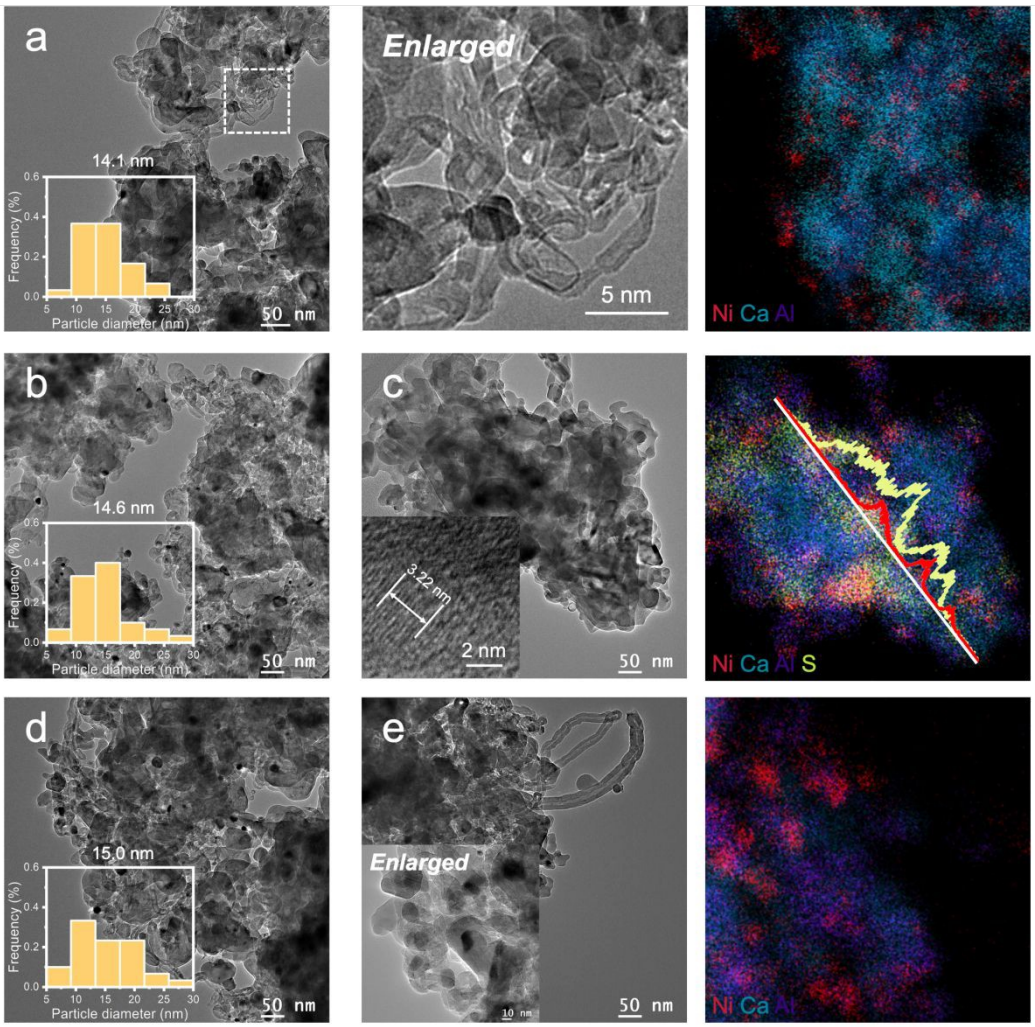

Fig. 11 TEM of cycled DFM.

(a) Cycled DFM with enlarged CNTs and EDX; (b) cycled DFM under 100 ppm SO_2-containing flue gas; (c) cycled DFM under 500 ppm SO_2-containing flue gas and EDX; (d) cycled DFM under 100 ppm NO_2-containing flue gas; (e) cycled DFM under 500 ppm NO_2-containing flue gas and EDX.

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The nature and structure of carbon deposits on cycled Ni5Al15Ca DFMs were further examined by Raman spectroscopy, as shown in Fig. 12. The DFM cycled without SO_2 or NO_2 exhibited two prominent peaks centered at approximately 1357 cm^{-1} (D band) and 1579 cm^{-1} (G band), corresponding to amorphous carbon and graphitic sp^2 carbon, respectively. The intensity ratio (I_D/I_G) was used to evaluate the degree of graphitization. In the absence of SO_2 and NO_2, the cycled DFM displayed an I_D/I_G value of 1.1, indicative of the formation of highly graphitic carbon structures such as carbon nanotubes, consistent with TEM observations. Upon exposure to 100 ppm SO_2, the I_D/I_G ratio increased to 1.6, likely due to partial deactivation of Ni active sites. For DFMs exposed to 500 ppm SO_2, neither D nor G bands were detectable, indicating an absence of detectable carbon deposition, which was consistent with the TEM and reactor data. Introduction of NO_2 during the CO_2 capture stage showed minimal effect on the type of carbon formed during the CH_4 dry reforming step. However, carbon deposition was evidently suppressed, as corroborated by fixed-bed reactor results, even though the Raman spectra did not indicate significant changes in the graphitization degree.

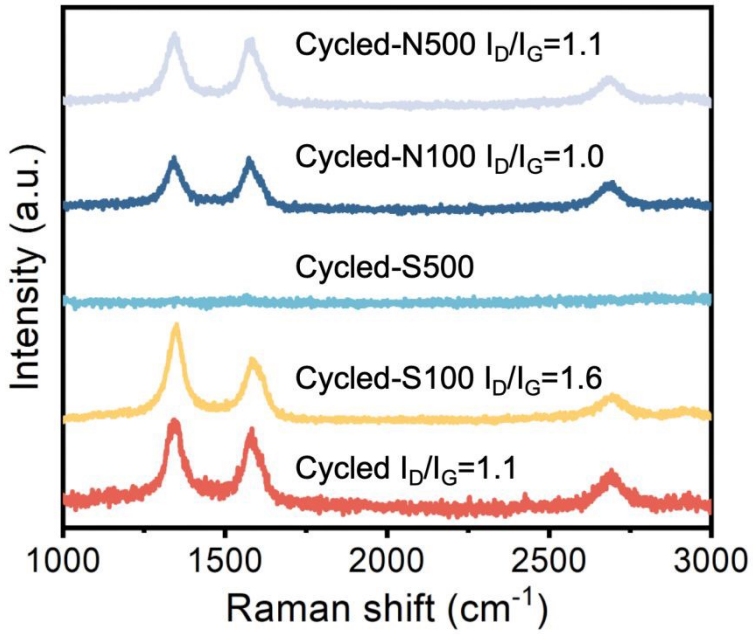

Fig. 12 Raman spectrum of cycled DFMs.

X-ray photoelectron spectroscopy (XPS) was conducted to gain insight into the surface elemental composition and chemical states of the cycled Ni5Al15Ca DFM, as shown in Fig. 13. Sulfur species were clearly detected on the surface after exposure to 100 ppm SO_2, with significantly intensified peaks under 500 ppm SO_2 conditions. Two characteristic S 2p signals at 163.2 eV and 172.4 eV were assigned to sulfide and sulfate species, respectively. Although only CaS was identified in the bulk phase by XRD, XPS analysis revealed that both sulfide and sulfate species were present on the surface in comparable proportions at lower SO_2 concentrations. Under 500 ppm SO_2, the surface was dominated by sulfide species, in agreement with the increased CaS content observed by XRD. In contrast, for the NO_2-treated DFM, no nitrogen species were detected on the surface after 10 cycles, suggesting that nitrogen-containing intermediates were fully decomposed or desorbed during the dry reforming process. This observation is consistent with both the elemental analysis and the absence of stable nitrogen-containing phases in the XRD results.

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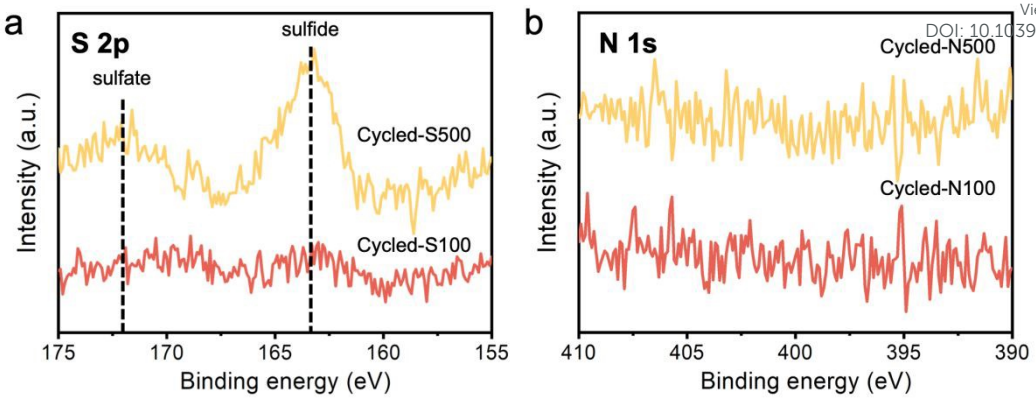

Fig. 13 XPS of cycled DFM.

(a) SO_2-containing flue gas condition and (b) NO_2-containing flue gas condition.

Based on the above experimental findings, a mechanism is proposed to elucidate the influence of SO_2 and NO_2 on the ICCU-DRM process. During the CO_2 capture stage, both SO_2 and NO_2 can be co-adsorbed by CaO alongside CO_2. The generated CaS and $CaSO_4$ species are thermally stable and persist into the subsequent CH_4 dry reforming stage, whereas calcium nitrates formed from NO_2 adsorption are thermodynamically unstable and decompose upon gas switching. The formation of CaS and $CaSO_4$ can act as physical barriers that suppress CaO sintering and thereby enhance the cyclic stability of the DFM. However, progressive accumulation of these sulfur species leads to the irreversible consumption of active CaO, reducing the theoretical CO_2 uptake capacity. In the case of NO_2, the decomposition of calcium nitrates during cycling may contribute to improved pore structure, offering potential benefits for gas diffusion. During the CH_4 dry reforming stage, both SO_2 and NO_2 induce part or total deactivation of the Ni active sites through the formation of surface coating layers. NO_2 and low concentrations of SO_2 result in partial deactivation, leading to preserved CO_2 conversion but a notably reduced H_2:CO ratio and suppressed carbon deposition. In contrast, high SO_2 concentrations cause near-complete deactivation of Ni sites, eliminating both CO and H_2 production. This mechanistic insight highlights the nuanced and concentration-dependent effects of flue gas pollutants on ICCU performance, providing important guidance for the development of sulfur- and nitrogen-tolerant DFM materials in realistic industrial applications.

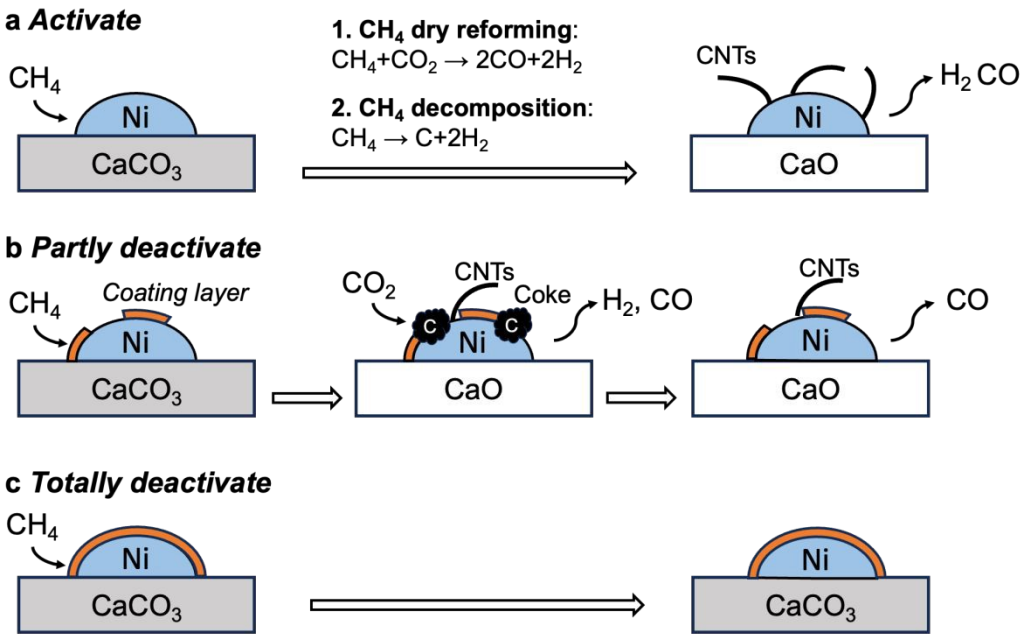

Fig. 14 Influence mechanism illustration of SO_2 or NO_2 pollutions in flue gas for ICCU-DRM.

3. Conclusions

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In this study, we systematically evaluated the influence of SO_2 and NO_2 in flue gas to the ICCU-DRM performance and uncover relevant mechanism. Fixed-bed reactor results revealed that low concentration of SO_2 (100 ppm) in flue gas showed minor influence to the CO_2 conversion, but can effectively inhibit the methane decomposition side reactions, therefore significantly reduce the carbon deposition. Moreover, the low concentration of SO_2 in flue gas can effectively improve the stability of CO_2 capture. However, with the increase of SO_2 concentration to 500 ppm, the adsorption capacity and catalytic reforming capacity of the DFMs decreased significantly, and the materials were significantly deactivated after 10 cycles. NO_2 in flue gas exhibited similar trend with SO_2 but at lower impact level. Characteristics revealed that both SO_2 and NO_2 induced a coating layer on the surface of Ni catalytic site, which reduced the catalytic performance of the Ni active site, and then affect the performance of the DFM. This study provided a solid foundation for the design and application of DFMs under realistic flue gas conditions.

4. Experimental section

4.1 Material synthesis

The typical Ni5Al15Ca DFM was synthesized by a sol-gel method. Calculated amount of 15.11 g $Ca(NO_3)_2{\cdot}4H_2O$ (Aladdin, 99.9%), 4.50 g $Al(NO_3)_3{\cdot}9H_2O$ (Aladdin, 99.9%), and 1.16 g $Ni(NO_3)_2{\cdot}6H_2O$ (Aladdin, 99.9%) were dissolved in 60 mL deionized water and stirred for 1 h. 15.36 g citric acid (Aladdin, 99.5 %) was then added to the solution with another 1 h. Then the mixture was heated to 90°C with oil bath. The mixture formed a wet-gel after ca. 5 h, which was subsequently aged overnight in an oven at 120°C to form the dry-gel. The dry-gel was then calcined in a muffle furnace at 850°C for 2 h with a ramp rate of 10 °C min^{-1}. The as-synthesized powder was granulated to 40–60 mesh size. Finally, the Ni5Al15Ca DFM was pretreated in H_2 at 700°C for 3 h.

4.2 Material characterization

The molar ratios of Ni, Al, Ca and S in DFM were calculated using ICP-OES (Agilent ICPOES730) after digestion in nitric acid. The N element was analyzed by elementary analyzer (EA, Thermo Scientific Flash Smart Analyzer). Crystal structure of DFM was measured by XRD (PANalytical Empyrean series) equipped with a Bragg-Brentano high-definition mirror. The data was collected within the 2theta range of 10–90° with a step size of 0.01303° and 50 s per step. SEM (JEOL JSM-9700F) was applied to characterize the morphology and element distribution of the materials. Morphologies of nanoparticles and element distributions were investigated by TEM (JEOL JEM-2100 Plus, operated at 200 kV) equipped with EDX. The surface area and pore volume of the materials were determined by N_2 physisorption (Micromeritics, ASAP 2460 analyzer), with the Brunauer-Emmet-Teller (BET) model (using the adsorption data) and Barrett-Joyner-Halenda (BJH) model (using the desorption data), respectively. XPS (SPECS) with Al Kα X-ray source and PHOIBOS 150 Analyzer was performed for surface element analysis. The C 1s peak of adventitious carbon was set at 284.8 eV to correct for any charge-induced shifts. H_2-TPR (Micromeritics, AutoChem II-2920 system) was performed to evaluate the reducibility of the DFM. Ca. 100 mg sample was pretreated at 800 °C under Ar atmosphere. After cooling to room temperature, the sample was reduced at a ramp rate of 10°C min^{-1} under 10% H_2/Ar from room temperature to 1000°C. The carbon capture capacity of DFM was evaluated by TGA (NETZSCH STA2500). Ca. 5 mg sample was placed in an alumina pan in the analyzer chamber and the weight signal was collected at 650°C under 15% CO_2/N_2.

4.3 Performance test of integrated carbon capture and methane dry reforming

The performance of integrated carbon capture and methane dry reforming (ICCU-DRM) was evaluated by a fixed-bed system. The gas analyzer (Cubic Ruiyi Instruments, Gasboard 3000) was used to analyzed the real-time concentration of gas. CO_2, CO and CH_4 was detected by non-dispersive infrared (NDIR) detector, while H_2 was detected by thermal conductivity detector (TCD). Briefly, ca. 200 mg DFM was placed in a quartz tube with an internal diameter of 8 mm. As for a typical ICCU-DRM test, the DFM was first pretreated under N_2 (50 mL min^{-1}) at 675°C to remove the adsorbed CO_2. Subsequently, the carbon capture stage was performed under 15%CO_2/N_2 (50 mL min^{-1}) at 650°C for 40 min. As for SO_2 and NO_2 containing flue gas, corresponding concentrations of SO_2 and NO_2 were mixed into the flue gas. The uncaptured CO_2 was purged by N_2 (50 mL min^{-1}) for 10 min. As for dry reforming stage, the DFM was exposed to 10% CH_4/N_2 (50 mL min^{-1}) at 675°C for 30 min, followed by purging by N_2 (50 mL min^{-1}) for 10 min. All working conditions repeated for 10 capture/conversion cycles to test the stability of the DFM. All experiments were operated at atmospheric pressure.

The CO yield in carbon capture stage, CO_2 uptake, CO_2 conversion, and H_2:CO ratio were calculated as below:

$$\text{CO yield in carbon capture stage (mmol g}^{-1}) = \frac{\int F^{\text{out}}_{\text{Cap, CO}}(t)\,\mathrm{d}t}{m_{\text{DFM}}}$$

$$\text{CO}_2\text{ uptake (mmol g}^{-1}) = \frac{\int [F^{\text{in}}_{\text{Cap,CO}_2}(t) - F^{\text{out}}_{\text{Cap,CO}_2}(t) - F^{\text{out}}_{\text{Cap,CO}}(t)/2]\,\mathrm{d}t}{m_{\text{DFM}}}$$

$$\text{CO}_2\text{ conversion (\%)} = \frac{\int F^{\text{out}}_{\text{Con, CO}}(t)/2\,\mathrm{d}t}{\int [F^{\text{out}}_{\text{Con, CO}}(t)/2 + F^{\text{out}}_{\text{Con, CO}_2}](t)\,\mathrm{d}t}$$

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$$H_2\text{:CO ratio (1)} = \frac{\int F^{out}_{Con,H_2}(t)\,dt}{\int F^{out}_{Con,CO}(t)\,dt}$$

where, *F* denotes the molar flow rate of the gas, Cap and Con refers to carbon capture stage and conversion stage. M_{DFM} represents the mass of DFM.

4.4 In situ XRD

In situ XRD experiments were conducted on the XRD (PANalytical, Empyrean Series) equipped with an XRK 900 reactor chamber from Anton Paar (Anton Paar, XRK-900). The DFMs were firstly in situ reduced at 700°C under a flow of 100 mL min^{-1} H_2 for 1 h, followed by purging in N_2. Subsequently, 100 mL min^{-1} 2000 ppm SO_2/15% CO_2/N_2 was introduced into the chamber for 90 min. After another 100 mL min^{-1} N_2 purge, 100 mL min^{-1} 20% CH_4/N_2 was introduced into chamber for 90 min. The XRD patterns were continuously recorded with 2theta of 20–45° with 2.5 min per scan.

Author contributions

H.Z., S.S. and B.Y. conceived the research project. B.Y. designed the experimental work. B.Y., M.Y. and Y.W. performed the experiments. B.Y. contributed to the in situ XRD experiments. Y.X. and X.B. assisted with the catalyst characterization. Data analysis and interpretation were discussed among all coauthors. B.Y., S.S. and H.Z. wrote the manuscript, with contributions from all authors.

Conflicts of interest

There are no conflicts to declare.

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Data availability statement

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