Structured Ni@NaA zeolite supported on silicon carbide foam catalysts for catalytic carbon dioxide methanation

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Abstract
Carbon dioxide (CO2) conversion is an important yet challenging topic, which helps to address climate change challenge. Catalytic CO2 methanation is one of the methods to convert CO2, however, it is limited by kinetics. This work developed a structured Ni@NaA zeolite supported on silicon carbide (SiC) foam catalyst (i.e., Ni@NaA-SiC), which demonstrated an excellent performance with a CO2 conversion of ~82%, being comparable to the corresponding equilibrium conversion, and CH4 selectivity of ~95% at 400°C. The activation energy for CO2 conversion over the 15Ni@NaA-SiC catalyst is about 31 kJ mol⁻¹, being significantly lower than that of the 15Ni@NaA pelletized catalyst (i.e., ~84 kJ mol⁻¹). Additionally, the structured catalyst was highly stable with sustained CO2 conversion at 78.7 ± 1.4% and selectivity to CH4 at 97.7 ± 0.2% over an 80 hr longevity test. In situ diffuse reflectance infrared Fourier transform spectroscopy-mass spectroscopy characterization revealed that catalysis over the structured catalyst proceeded primarily via the CO free mechanism.

KEYWORDS
CO2 methanation, in situ characterization, silicon carbide (SiC) foam, structured catalyst, zeolite
1 | INTRODUCTION

Carbon dioxide (CO₂) emissions from many sources such as biogas, natural gas, and coal combustion are the major contributor to the greenhouse gases (ca. 82%), being the primary reasons for the serious global warming and climate change issues. Therefore, many efforts have been made recently to develop highly efficient CO₂ capture and utilization (CCU) technologies for reducing and converting CO₂ emissions, fighting against the urgent environmental issues. The power-to-gas (P2G) process is an energy storage and conversion technology that can convert the surplus sustainable energy into gas fuel (i.e., hydrogen, H₂) effectively, which can be subsequently used for CO₂ conversion (to methane). P2G relies on water electrolysis (for sustainable H₂ production) and CO₂ hydrogenation (the so-called catalytic CO₂ methanation for producing methane, CH₄, Equation 1). Therefore, P2G enables the sustainable production of economical viable H₂ to hydrogenate CO₂ into CH₄, which can be either directly injected into the existing gas grid or used as a feedstock for the production of other value-added chemicals (e.g., via methane aromatization into aromatics). Although catalytic CO₂ methanation is thermodynamically favorable at low temperatures, it suffers from the kinetic limitation due to the high stability of CO₂ molecules. Accordingly, elevated temperatures (at ca. 200–750 °C) are normally required to activate the catalyst to enable the hydrogenation of CO₂. In addition, CO₂ methanation is highly exothermic (Equation 1) and the development of local hotspots is common along the catalytic packed bed, being one of the main reasons for catalyst sintering and deactivation. Moreover, conventional fixed bed reactors with packed catalyst pellets normally suffer from poor heat transfer and insufficient heat dissipation, which are likely to result in thermal runaway, and thus associated deactivation and safety issues.

To overcome the limitation of conventional packed beds, structured catalysts such as monoliths, structured fibrous networks, and structured foams have been studied to mitigate the effect by heat/mass transfer on chemical transformation and separation processes, including catalysis such as catalytic CO₂ methanation. For example, Ni catalysts supported on ceria-zirconia coated foams (including open-cell silicon carbide (SiC), alumina and aluminium foams) and carbon felt were developed and assessed for promoting catalytic CO₂ methanation, and heat regulation. Importantly, in situ infrared thermography was employed to examine the surface temperatures and development of hotspots due to the exothermicity of the reaction on structured catalysts based on different foams, showing that both SiC and aluminium foams (with the intrinsically high thermal conductivity) presented the improved heat transfer than alumina foams. In addition, electromagnetic induction heating was applied to regulate heat transfer in structured catalysts (e.g., Ni supported on carbon felt) for catalytic CO₂ methanation process, being able to improve heating/cooling rates with uniform heating environments and high energy efficiency.

SiC open-cell foams have been demonstrated as ideal candidates to develop structured catalysts for addressing the mass and heat transfer limitations in many challenging exothermic reactions (e.g., methanol-to-propylene (MTP) reaction), offering many advantages such as high surface-to-volume ratios, improved mass and heat transfer coefficient, as well as low bed pressure-drops. The surface of SiC foams can be easily functionalized using inorganic materials, especially zeolites, via many routes such as washing coating and dispersion based direct synthesis methods. Accordingly, the surface functionalized SiC foams can be used directly as catalysts or structured catalyst supports (for supporting metal active sites), enabling the process intensification of heterogeneous catalysis under continuous-flow conditions.

Recently, Ni catalysts supported on zeolite 5A were developed for sorption-enhanced CO₂ methanation due to their high capability of water uptake (e.g., 23 g water kg⁻¹ of zeolite at 21 °C and 53% relative humidity). The developed catalyst (e.g., Ni/zeolite 5A) demonstrated significantly higher CH₄ yield (e.g., nearly 100%) than the commercial catalysts (i.e., Ni supported on silica/alumina). Experimental results revealed that in situ adsorption of water on zeolite from the reaction stream improved the catalysis greatly due to the Le Chatelier principle. In this work, we present the development of the structured Ni catalyst supported on LTA zeolite (sodium form, NaA) coated SiC foams (i.e., Ni@NaA-SiC, as shown Figure 1) for intensifying catalytic CO₂ methanation. The novelty of the work lies in the combination of SiC foams and a hydrophilic NaA coating to enhance the Ni catalyzed CO₂ methanation by (a) reducing the effect of global mass and heat transfer and (b) shifting the equilibrium towards CH₄ formation. The development of NaA-SiC composite support was investigated, specifically the systematic study of the effect of synthesis parameter (e.g., repeated cycles of the hydrothermal synthesis) on the morphological property of the NaA coating supported on the surface of SiC. After Ni impregnation on the selected NaA-SiC (which was prepared with 2 cycles of the hydrothermal synthesis), kinetic study of catalytic CO₂ methanation was performed. Finally, in situ diffuse reflectance infrared Fourier transform spectroscopy-mass spectroscopy (DRIFTS-MS) investigation of the catalytic system was performed to enable the mechanistic understanding of the catalysis over the developed structured catalyst.

2 | EXPERIMENTAL

2.1 | Synthesis of the structured Ni@NaA-SiC catalyst

NaA zeolite seeds were prepared according to a previously reported method. The detailed experimental procedure of preparing the NaA seeds is described in the Supporting Information (SI). To prepare the NaA seeds solution, 0.317 g hydroxypropyl cellulose (99%, Aldrich)
was firstly added in 30 ml deionized (DI) water under sonication for 30 min. Subsequently, 1.5 g NaA seeds were added into the solution and ultra-sonicated for 20 min to obtain the seed suspension. The dispersion of the seed suspension on SiC foam with open porosity of ca. 70% was achieved by dip-coating (1 min each, repeated for 10 times). The seeded SiC foam was dried at 80°C overnight in order to remove the water from Ni@NaA-SiC. After seeding, NaA zeolite was firstly added in 30 ml deionized (DI) water under sonication for 4 hr in a 45 ml Parr vessel using a synthesis gel with molar composition of 4Na:2Si:2Al:150H2O (method of preparing the synthesis gel is described in the SI). After the synthesis, the sample was rinsed by DI water for several times, and dried at 80°C overnight to obtain NaA coated SiC foams. The hydrothermal synthesis was repeated (up to three times) to improve the NaA dispersion on SiC foams, and the relevant samples were denoted as NaA-1-SiC, NaA-2-SiC, and NaA-3-SiC, respectively. The Ni@NaA-SiC catalysts were prepared by supporting Ni on NaA-2-SiC using an incipient wetness impregnation (IWI) method (the theoretical Ni loading based on the weight of NaA coating was 10, 15, and 20 wt%, respectively). Specifically, NaA-2-SiC support was impregnated with the nickel nitrate (Ni(NO3)3, 99.999% trace metal basis, Aldrich) aqueous solution in a glass tube (10 mm i.d.) overnight. After impregnation, the samples were dried at 100°C overnight in order to remove the water from Ni@NaA-SiC catalysts. The catalysts have been denoted according to their theoretical Ni loading, that is, xNi@NaA-SiC (x = 10, 15, and 20). In addition, control catalysts with a nominal Ni loading of 15 wt% were prepared using bulk NaA zeolite and bare SiC foam as supports, that is, the 15Ni@NaA and 15Ni@SiC catalysts, respectively. The actual metal loading was measured using inductively coupled plasma optical emission spectroscopy (ICP-OES, Quant PQ 900), and the relevant results are presented in Table S2 in the SI. Prior to ICP-OES, the sample (~25 mg) was mixed with 12 ml aqua regia and digested in an ETHOS UP microwave digester for 20 min under 220°C.

2.2 Characterization of materials

Powder X-ray diffraction (XRD) analysis was carried out on a Proto AX-ray diffractometer with a nickel absorber (0.02 mm, Kβ = 1.3923 Å) producing Kα radiation (Kα1 = 1.5406 Å). XRD data was collected at 2θ = 5°–70°. Nitrogen (N2) adsorption–desorption isotherms at –196.15°C were measured using a Micromeritics ASAP 2020 analyzer. Before N2 physisorption, all samples were degassed at 300°C overnight (~12 hr). The specific surface area was calculated using the Brunauer–Emmett–Teller (BET) method. Scanning electron microscopy (SEM) images of the samples were obtained using a FEI Quanta 250 ESEM with a high voltage of 15 kV, and energy dispersive X-ray (EDX) spectroscopy on an Oxford Ultim Max system was used to perform EDX mapping analysis. All samples were coated with platinum before SEM analysis. H2 pulse chemisorption for determining the dispersion and active surface area of Ni was performed on a Micromeritics AutoChem II 2920 instrument. In H2 pulse chemisorption measurement, the sample was prerduced at 450°C (for 1 hr) under a 10% H2/Ar flow at 30 ml min⁻¹, then cooled down to 50°C and purged for 30 min to clean the catalyst surface (all under Ar at 30 ml min⁻¹). At 50°C under Ar (30 ml min⁻¹), as the carrier gas to protect thermal conductivity detector [TCD], H2 pulse chemisorption was started by pulsing of a mixture of 10% H2 in Ar (loop volume = 0.5 ml) to the sample, as shown in Figure S2 (exemplified by the 15Ni@NaA-SiC catalyst). The measurement was performed at 50°C to minimize the H2 physisorption on Ni surface. By comparing the TCD signal due to chemisorption on the catalyst with that from the experiment on saturated catalyst (with the same loop volume), determination of the amount of chemisorbed H2 directly was achieved. H2 temperature-programmed reduction (TPR) was investigated using a Quanta Chrome ChemBET Pulsar TPR/TPD instrument. About 50 mg of a sample was pretreated at 250°C for 30 min under a helium flow to clean the catalyst surface, and then cooled down to room temperature (RT). H2-TPR was carried out in a gas mixture flow of 5%H2/Ar from 30–900°C with a heating rate of 10°C min⁻¹.
2.3 Catalytic CO₂ methanation

Catalytic CO₂ methanation over the structured Ni@NaA-SiC catalysts was carried out under continuous-flow conditions at atmospheric pressure, and the experimental rig is shown in Figure S1. The structured Ni@NaA-SiC catalyst (9 mm O.D. × 25 mm length, volume: 1.6 cm³, amount of Ni@NaA phase: ~200 mg) was loaded in the middle of a stainless-steel reactor (10 mm O.D. × 120 mm length, as shown in Figure S1 in the SI) which was equipped with a thermocouple to monitor the actual temperature of the catalyst bed. The catalysts were wrapped with graphite tape to avoid the wall effect that is, channeling. Before the reaction, the catalyst was reduced in a 20% H₂/Ar flow at 500°C for 5 h. Thereafter, a gas mixture with a composition of H₂/CO₂ = 4 (flow rate = 50 ml standard temperature and pressure (STP) min⁻¹, gas hourly space velocity (GHSV) = 1875 hr⁻¹) was introduced into the reactor via two mass flow controllers (Bronkhorst®, F-201CV-500-RAD-11-V). Catalysis was performed at 250–500°C. At each temperature, CO₂ methanation achieved steady state after ~30 min time-on-stream (TOS). After that, the gas composition in the outlet of the reactor was measured by gas chromatograph (GC, PerkinElmer, Clarus® 590) equipped with an elite-carbon molecular sieve packed column (N9303926), methaniser, TCD and flame ionization detector (FID). Additionally, catalytic performances of reference 15Ni@NaA and 15Ni@SiC catalysts and bulk SiC support (total volume of all catalysts and bulk SiC support: 1.6 cm³, 15Ni@NaA with amount of ~200 mg diluted by SiO₂ pellets) were also evaluated using identical experimental procedures. Details regarding the sampling and calculations of conversion and selectivity are presented in the SI.

In order to determine the specific reaction rate, kinetic studies were performed. To avoid the diffusion limitation (to a large extent) and obtain the intrinsic kinetics, small amount of catalysts (i.e., structured foam catalyst: 9 mm O.D. × 5 mm length, pelletized 15Ni@NaA catalyst with amount of ~30 mg diluted by SiO₂ pellets, volume: 0.3 cm³) were used in the kinetic studies (flow rate = 50 ml (STP) min⁻¹, GHSV = 9,375 hr⁻¹), and the conversion was kept below 20%. Specific reaction rates were calculated using Equation 2:

\[ r_{CO_2} = \frac{X_{CO_2} \times P^{in}_{CO_2}}{W_{cat} \times C_{Ni}} \]  

(2)

where \( r_{CO_2} \) is the reaction rate of CO₂ (mol s⁻¹ g-cat⁻¹), \( X_{CO_2} \) is the conversion of CO₂, \( P^{in}_{CO_2} \) is the molar flow rate of CO₂ in the inlet of the reactor (mol s⁻¹), \( W_{cat} \) is the mass of the catalyst (g), \( C_{Ni} \) is the actual Ni content of the catalyst (by ICP-OES, as shown in Table S2).

2.4 In situ DRIFTS-MS studies of catalytic CO₂ methanation over Ni@NaA-SiC catalyst

In situ DRIFTS characterization of the surface chemistry during the catalysis was performed using a Bruker Vertex 70 FTIR spectrometer equipped with a liquid N₂-cooled detector, which has been detailed elsewhere. In situ DRIFTS spectra were recorded at every ~56 s with a resolution of 4 cm⁻¹ and analyzed with the OPUS software. Prior to DRIFTS analysis, the 15Ni@NaA-SiC catalyst was ground and loaded into a ceramic crucible in the IR cell, and pretreated at 500°C for 1 h in a 10% H₂/Ar flow. Different gas mixtures controlled by electronic mass flow controllers (Brooks) were introduced into the DRIFTS cell. The gases at the outlet of the DRIFTS cell were analyzed by a MS in order to record the evolution of the m/z = 44 (CO₂), 2 (H₂), 15 (CH₄), 28 (CO), and 18 (H₂O) with the response time of the MS being less than 1 s. For measuring the evolution of the DRIFTS spectra during catalysis, gas mixture with a total flow rate of 50 ml min⁻¹ (10% CO₂ + 40% H₂ diluted in Ar) was introduced into the cell, and the DRIFTS spectra were recorded by ramping the temperature of cell from 40 to 400°C at 5°C min⁻¹. Regarding the experiments with DRIFTS at a constant temperature, the same gas mixture (10% CO₂ + 40% H₂ diluted in Ar) was introduced into the DRIFTS cell at different temperatures of 300, 350, and 400°C, and the DRIFTS spectra were recorded for 15 min. For the transient experiments, gas mixtures at a constant flow rate of 50 ml min⁻¹ was switched between 10% CO₂ in Ar, 10% CO₂ + 40% H₂ in Ar, and 40% H₂ in Ar, and introduced to the cell (5 cycles).

3 RESULTS AND DISCUSSION

3.1 Characterization of materials and catalytic CO₂ methanation performances over different catalysts

The developed NaA zeolite supported on open-cell SiC foam composites (NaA-SiC) were comprehensively characterized using various techniques (i.e., SEM, N₂ physisorption, and XRD), and the results are presented in Figures 2 and 3, and Table 1. After seeding, as shown in Figure S2, SEM analysis show that a uniform layer of NaA seeds (with particles size of ~400 nm) was dispersed on the surface of SiC foams. Figure 2 shows the morphology of NaA zeolite phases on SiC foam after the repetitive secondary hydrothermal synthesis. After one synthesis (i.e., NaA-1-SiC), as shown in Figure 2a,d,g, the NaA coating consisting of inter-grown crystalline aggregates (with sizes of 4–6 μm) was formed on the surface of SiC foam. However, the close observation of the coating (Figure 2d) shows the presence of cracks/holes in the NaA coating, as indicated by the red dashed circles in Figure 2d. By repeating the secondary hydrothermal synthesis once (to give NaA-2-SiC), the amount of NaA coating on SiC foam in NaA-2-SiC increased significantly. Accordingly, a dense NaA layer with relatively large inter-grown crystals (with sizes of 6–9 μm, as shown in Figure 2e,h) was prepared. Small NaA crystals of <1 μm were formed on the surface of NaA-2-SiC (Figure 2e,h), indicating the re-nucleation and growth of NaA zeolites. After three repetitive hydrothermal synthesis (to give NaA-3-SiC), the resulting NaA layer (Figure 2c,f,i) nearly clogged up the open-cells of SiC foam, which can potentially impede the gas flow through the structured composite materials, and hence increasing bed pressure drop (as shown in Figure S4). Specifically, the
averaged pressure drop of the NaA-3-SiC composite ($3.5 \times 10^5 \pm 4.7 \times 10^7$ Pa m$^{-1}$) increased by $\sim 10.1\%$ compared to that of NaA-2-SiC ($3.2 \times 10^5 \pm 2.6 \times 10^7$ Pa m$^{-1}$). The findings from SEM analysis revealed that the repetitive hydrothermal synthesis (after seeding) could significantly affect the morphology NaA zeolite coating, as well as the amount, which was evidenced by the weight gain of the composites (i.e., $\sim 7.5$ wt% after one synthesis vs. $\sim 16.5$ wt% after three synthesis, as shown in Figure S5).

Comparative XRD patterns of NaA-SiC composites with reference to NaA seeds and bare SiC foam are presented in Figure 3a. In addition to the characteristic peaks of SiC phase (indicated by the ♣ symbol), the characteristic peaks of NaA phase (at $2\theta = 7.2, 10.5, 12.5, 24.1, 27.2$ and $30^\circ$, respectively, indicated by the * symbol) were observed in the XRD patterns of the NaA-SiC composites, matching well with that of NaA seeds. Detailed examination of XRD patterns of NaA zeolite coatings at $2\theta = 5-30^\circ$ (Figure 3b) shows that the intensity of characteristic peaks of the NaA coating on SiC foam increased after the repetitive synthesis, which is in line with the results above by SEM and weight gain measurements as well (as discussed above).

Figure 3c shows the N$_2$ physisorption isotherms of bare SiC foam, NaA seeds and NaA-2-SiC composite, and the corresponding textual and structural properties of the materials are summarized in Table S1. The BET surface area ($S_{BET}$) of bare SiC foam is significantly low (i.e., $\sim 0.1$ m$^2$ g$^{-1}$). SiC foams contain macroscopic cellular structure, and their macro-pore properties cannot be probed by N$_2$ physisorption. NaA seeds (as shown inset in Figure 3c) exhibited the isotherm similar to type II (b) with a hysteresis loop in the $p/p_0$ range of 0.6–0.8. 40 The NaA-2-SiC composite shows the similar isotherm to that of NaA seeds, but the specific quantity adsorbed is considerably lower (Table S1).
This is reasonable since the determination of the specific values of the composite included the weight of SiC foam support. Considering the trade-off between the coating quality and the possible penalty due to pressure drop, NaA-2-SiC composite was selected for supporting Ni catalyst, characterization and catalytic evaluation.

The NaA-2-SiC composite was used as support for preparing the Ni@NaA-SiC catalysts with different theoretical Ni loadings of 10 wt% (10Ni@NaA-SiC), 15 wt% (15Ni@NaA-SiC) and 20 wt% (20Ni@NaA-SiC). According to EDX (Figure 4), Ni element is present in all the catalysts under study (before reduction). As shown in Figures 4a–f, the amount of Ni element (yellow) increases notably as the Ni nominal content in the Ni@NaA-SiC catalysts was increased from 10 to 20 wt%. Visually, EDX analysis shows that the presence of Ni element on NaA, regardless bulk NaA or NaA-SiC composite, is generally uniform. The distribution of other elements of Na, Al, and Si in the NaA zeolite phase of 15Ni@NaA-SiC and 15Ni@ catalysts is presented in Figure S6, showing the comparable Si/Al molar ratio of ~1.2. However, H₂ pulse chemisorption analysis (as summarized in Table 1) shows that the Ni dispersion and metallic surface area in the 15Ni@NaA-SiC catalysts (i.e., 1.02% and 6.76 m² g⁻¹) were significantly higher than that of 15Ni@NaA (i.e., 0.6% and 3.98 m² g⁻¹).

The findings revealed that, in comparison with the bulk NaA zeolite, the structured NaA supported on SiC foam could possibly promote the metal dispersion, being beneficial to the catalysis. Specifically, in IWI process, the contacting efficiency between the catalyst support and Ni precursor is key to determine the metal dispersion and particle size in the developed catalyst. In this work, for structured NaA-SiC composite supports, thin layer of NaA zeolite coating on the surface of SiC foam has relatively high geometric surface area. Therefore, the contacting efficiency between NaA zeolite coating and Ni precursor in IWI could be higher than that of the conventional NaA zeolite pellet, leading to a good dispersion of Ni species in the zeolite coating. Conversely, for NaA zeolite pellets, in IWI, Ni precursor had to diffuse slowly and contact with the zeolite support under continuous stirring, which could easily result in the aggregation of Ni phases in the framework of NaA, leading to relatively low metal dispersion. However, for NaA-SiC composite, a relatively high Ni precursor concentration (i.e., 20 wt% theoretical loading) also caused a significant reduction in metal dispersion and metallic surface area to 0.14% and 0.91 m² g⁻¹, respectively. Reduction behaviors of the catalysts under investigation was probed by H₂-TPR (as shown in Figure S7). The H₂-TPR profile of the 15Ni@NaA catalyst presented a wide peak in the region of 300–700°C with a sharp peak located at 450–550°C, which can be attributed to the reduction of NiO species on NaA support, being consistent to previous results in the literature. Similar reduction behaviors were measured for the structured catalysts with different Ni contents (i.e., 10Ni@NaA-SiC, 15Ni@NaA-SiC, and 20Ni@NaA-SiC) as well. However, TCD signals are relatively weak which was due to the dilution of SiC support of the structured catalysts. Accordingly, based on the H₂-TPR results, the reduction

**TABLE 1** Metal dispersion and metallic surface area of the Ni@NaA-SiC and Ni@NaA catalysts by H₂ pulse chemisorption

| Catalysts   | Metal dispersion (%) | Metallic surface area (m² g⁻¹) |
|-------------|----------------------|-------------------------------|
| 10Ni@NaA-SiC | 1.09                 | 7.27                          |
| 15Ni@NaA-SiC | 1.02                 | 6.76                          |
| 20Ni@NaA-SiC | 0.14                 | 0.91                          |
| 15Ni@NaA     | 0.60                 | 3.98                          |

Abbreviation: SiC, silicon carbide.
temperature of 500°C was used for the catalytic performance evaluations and in situ DRIFTS-MS studies.

The performance of the catalysts in CO₂ methanation was assessed under thermal conditions, as shown in Figure 5a,b and S8, respectively. The bare SiC foam and the 15Ni@SiC catalyst showed insignificant activity under the conditions used, that is, CO₂ conversions of <10% at >300°C and no selectivity to CH₄, while the 15Ni@SiC catalyst showed the selectivity to CO of 35–45% at >300°C (Figure S8). Over the range of temperatures studied, the structured Ni@NaA-SiC catalysts showed relatively high activity (regarding the CO₂ conversion), as well as the selectivity to CH₄, being significantly better than that of the 15Ni@SiC catalyst. It can be concluded that the NaA zeolite layer is critical to greatly improve the loading and dispersion of Ni active sites, and hence the activity and selectivity. The onset temperatures of the catalysis over the structured catalysts were measured at 225°C, being comparable to that of the conventional packed bed with the 15Ni@NaA pellets (i.e., ~250°C). Specifically, at low temperature of <400°C (Figure 5b), the CH₄ selectivity of the structured catalysts (>85%) are higher than that of 15Ni@NaA pellet (55–75%). For the structured catalysts, an increase in Ni loading was found to improve both the absolute CO₂ conversion and selectivity to CH₄, which could be possibly attributed to the higher amount of Ni@NaA phase in the 20Ni@NaA-SiC catalyst. Although the volume of different structured catalysts was identical (i.e., 1.6 cm³), the Ni amount in the catalysts could be slightly different, which could increase with an increase of theoretical Ni loadings. Additionally, at relatively high temperatures of >400°C, all catalysts demonstrated high CO₂ conversions (e.g., ~80%), which are slightly higher than the corresponding theoretical thermodynamic equilibrium conversion (purple dashed line, calculated using Aspen Plus 8.0). At high temperature of >400°C (Figure 5b), all catalysts presented low selectivity to CO (<10%), suggesting the possible occurrence of reverse water-gas shift (RWGS, CO₂ + H₂ ⇄ CO + H₂O) reaction in the system. Conversely, the 15Ni@NaA catalyst only showed high selectivity to CH₄ (i.e., >95%) at high temperatures of >350°C. The improved catalytic performance of the structured catalysts can be attributed to the use of SiC foam, which can mitigate the effects of the global mass and heat transfers on the reaction. These aspects have been previously investigated and proved using both simulation and experimental methods. Regarding the heat transfer improvement promoted by SiC foams, previous work has shown that the structured SiC foam catalyst (e.g., ZSM-5/SiC) enabled a more uniform temperature distribution across the bed for the MTP process in comparison with the conventional packed beds, such as the packed bed based on ZSM-5 zeolite pellets, which was attributed to the relatively high thermal conductivity of SiC foam (e.g., 14 W m⁻¹ K⁻¹ at 773 K).²¹

The specific reaction rate of different catalysts was calculated using absolute CO₂ conversions measured in kinetic experiments, which are presented in Figure 5c. The 15Ni@NaA-SiC catalyst showed a specific reaction rate for CO₂ conversion of ~1.9 x 10⁻⁵ mol s⁻¹ gcat⁻¹, being higher than that of the pelletized 15Ni@NaA catalyst (ca. 0.8 x 10⁻⁵ mol s⁻¹ gcat⁻¹), which could be attributed to the difference in the mass of Ni species in the two catalysts. Due to (a) the same bed volume used for the catalysis in kinetic experiments and (b) thin zeolite coating layer on SiC foams,
the actual mass of Ni phase in the structured 15Ni@NaA-SiC catalyst was lower than that in the 15Ni@NaA catalyst. Therefore, according to Equation 2, the 15Ni@NaA-SiC and 15Ni@NaA catalysts have the same molar flow rate of CO₂ in the inlet of the reactor and comparable Ni loading (Table S2), and the 15Ni@NaA-SiC catalyst has a higher CO₂ conversion than 15Ni@NaA, the relatively high specific rate presented by 15Ni@NaA-SiC can be explained. Additionally, the contacting efficiency of the structured catalysts is also expected better than that of the conventional packed bed.²²

Arrhenius plots were used to calculate the activation energy (E_a) for the CO₂ conversion using kinetic data (Table S3), as shown in Figure 5d. The extracted parameters are listed in Table 2, showing that the structured Ni@NaA-SiC catalysts have
the calculated $E_A$ values in a range of 31–53 kJ mol$^{-1}$, which are lower than that of the pelletized 15Ni@NaA catalyst (i.e., ~84 kJ mol$^{-1}$). Specifically, for the structured Ni@NaA-SiC catalysts, the macroscopic cellular structure of SiC foams could minimize the external mass transfer,$^{13,21,22}$ while the thin coating of NaA zeolite on the surface of SiC foam could reduce the internal diffusion resistance within the catalytic layer. Consequently, the lower activation energies of the structured Ni@NaA-SiC catalysts, in comparison with the conventional 15Ni@NaA catalyst, can be attributed to the improved transport phenomena and metal dispersion (Table 1), being beneficial to readily activate the catalysis.

The long-term stability of the 15Ni@NaA-SiC catalyst for catalytic CO$_2$ methanation was also evaluated at 400 °C, and the results are presented in Figure 6. Over 80 hr TOS, the key indicators of its catalytic performance remained stable as a function of TOS with the CO$_2$ conversion at 78.7 ± 1.4%, CH$_4$ selectivity at 97.7 ± 0.2% and CO selectivity at 2.2 ± 0.2%, demonstrating the potential of the developed structured catalysts for practical CO$_2$ methanation in P2G. Since water is the co-product of the catalysis, at high temperatures, the hydrothermal stability of the zeolite coating needs to be evaluated. Previously, Ni catalysts supported on zeolite A (pellets) were developed for sorption-enhanced CO$_2$ methanation due to their high capability of water uptake (e.g., 23 g$_{\text{water}}$ kg$_{\text{zeolite}}^{-1}$ at 21 °C and 53% relative humidity).$^{32-37}$ The developed catalyst (e.g., Ni/zeolite 5A) demonstrated the robustness of zeolite A as the catalyst support for the catalysis, that is, being able to be regenerated via a simple drying step (under H$_2$ or air) between methanation cycles,$^{36}$ which showed reasonable stability of zeolite A as the catalyst support for CO$_2$ methanation. However, further efforts are still needed to assess the developed structured catalyst for extended TOS (e.g., 500 hr) under conditions relevant to practical applications (e.g., in the presence of water and/or H$_2$S) in order to evaluate the actual stability of the developed catalyst, especially, the hydrothermal stability of the zeolite coating.

### 3.2 In situ DRIFTS-MS study of catalytic CO$_2$ methanation over the 15Ni@NaA-SiC catalyst

The mechanisms of catalytic CO$_2$ methanation over different catalysts have been previously researched by different methods.$^{2,5,42-45}$ In this work, comparative in situ DRIFTS-MS studies of CO$_2$ methanation over the catalysts under investigation were further performed to see whether or not the presence of SiC foam might affect the surface reactions. The first sets of experiments were performed for the structured catalyst of 15Ni@NaA-SiC as a function of the reaction temperature. As shown in Figure 7, by ramping the temperature from 30 to 400 °C (10% CO$_2$ + 40% H$_2$ diluted in Ar), the following surface changes were observed: (a) the intensity of the IR band related to hydroxyl groups (at 1,650 cm$^{-1}$ and 3,500–3,800 cm$^{-1}$, corresponding to the adsorbed water molecules and surface hydroxyl groups in NaA) diminished progressively; (b) the IR band at 2,349 cm$^{-1}$ (which is related to the gas phase CO$_2$, shaded by the green rectangle) disappeared gradually, indicating the consumption of CO$_2$ due to the reaction over the catalyst; (c) the IR band at 1,566 cm$^{-1}$ (which could be attributed to monodentate carbonates adsorbed on extra frame-work aluminium of NaA zeolite or Ni$^0$ species$^{43}$) appeared progressively at 100–300 °C, then diminished gradually by increasing the temperature up to 400 °C; (d) the C-H vibration of CH$_x$ species (which is characterized by the IR band at 3,000 cm$^{-1}$, shaded by the blue rectangle) appeared gradually at temperatures higher than 300 °C.$^2$ Additionally, in situ DRIFT study of the 15Ni@NaA catalyst in the catalysis was also carried out (Figure S9), showing the comparable spectra to the structured catalysts under the same conditions. The findings from the in situ DRIFTS characterization (as a function of the reaction temperature) suggest that (a) SiC foam support did not alter the surface reaction and (b) the hydrogenation of monodentate species on Ni surface could be the rate

### Table 2 Kinetic parameters obtained from the kinetic analysis of the catalysis over the catalysts under study

| Catalysts        | $E_A$ (kJ Mol$^{-1}$) | $R^2$ |
|------------------|-----------------------|-------|
| 10Ni@NaA-SiC     | 53                    | 0.98  |
| 15Ni@NaA-SiC     | 31                    | 1.00  |
| 20Ni@NaA-SiC     | 45                    | 0.99  |
| 15Ni@NaA         | 84                    | 0.99  |

Abbreviation: SiC, silicon carbide.
determining step during the CO₂ methanation. Hence, in situ DRIFTS characterizations of CO₂ methanation under the isothermal conditions were also performed in order to identify the key reactive surface species.

Under isothermal conditions at 300, 350, and 400 °C (dwell time = 15 min for each condition), the surface species on the 15Ni@NaA-SiC catalyst were probed explicitly. The reaction profiles were monitored by MS during DRIFTS characterization, as shown in Figure 8. It was found that, at a constant temperature, the system reached steady state at ca. five minutes after the start-up based on the MS profiles associated with the m/z values of 2, 15, and 44, corresponding to H₂, CH₄, and CO₂, respectively (m/z = 28 signals were also detected during the catalysis by MS, which could be assigned to species from CO₂ fragmentation and CO from the catalysis, and hence discussion on it was not made). It should be noted that the breakthrough time of water (m/z = 18) in the catalytic system is relatively longer than that of other gases, indicating the sorption enhanced CO₂ methanation due to the good water adsorption capability of NaA zeolite, being in line with the findings reported previously. Specifically, previous findings demonstrated that the regeneration of these structured catalysts was possible via a drying step using either reducing (e.g., H₂) or oxidizing gas (e.g., air). However, future efforts are still needed to demonstrate the hydrothermal stability of the developed catalyst (especially the stability of zeolite framework) under flowing steam conditions at high temperature > 300 °C. As observed in Figure 8, in situ DRIFT spectra showed the formation of surface formates and carbonates on catalyst under different isothermal conditions. Under steady-state conditions, by comparing the spectra at three temperatures, the band intensity of surface monodentate carbonates (1,566 cm⁻¹) decreased significantly as a function of reaction temperature, while that of CH₄ species (3,000 cm⁻¹) become stronger. In addition, although it is rather weak, the IR band intensity of monodentate formates adsorbed onto Ni⁰ (1,653 cm⁻¹) remained constant. As shown in Figure 8, under isothermal condition at 400 °C, adsorbed linear carbonyl species on metallic Ni were not identified in the range of 1800–2080 cm⁻¹, indicating that CO₂ might not dissociate directly on the surface of Ni⁰ species. Therefore, the findings suggested that the CH₄ production in the catalysis with the formation of surface monodentate carbonates as the key intermediate, being consistent to previous findings. The corresponding MS profiles also show that the CH₄ production was preferred by operating the system under isothermal conditions at relatively high temperatures, that is, the intensity of produced CH₄ (m/z = 15) under steady-state increased significantly from ca. 1.25 × 10⁴ to 2.40 × 10⁵ as temperature increased from 300 to 400 °C.

In order to further identify the determining step during the reaction, the catalysis over the 15Ni@NaA-SiC catalyst was studied under cycling transient conditions at 400 °C, in which the surface dynamics...
and bulk gas composition of the system was probed in situ by DRIFTS-MS with the periodically switched feed streams between 10% CO₂/Ar and 10% CO₂/40% H₂ /Ar. As shown in Figure 9, under pure CO₂ stream, IR band at 1,566 cm⁻¹ is observed, confirming the formation of monodentate carbonate species adsorbed on the NaA zeolite surface. On switching CO₂ to the CO₂/H₂ mixture, the MS showed an instantaneous increase in the CH₄ signal, confirming the facile formation of CH₄ due to the quick surface reaction between the monodentate carbonates with dissociated H₂ on the surface of Ni⁰ species, which is accompanied by the disappearance of the IR bands at 1,566 and the appearing of weak IR band at 1,653 cm⁻¹ (i.e., the monodentate formates adsorbed on Ni⁰ species), respectively, as well as the emergence of the IR band at 3,000 cm⁻¹ (CHₓ species), being consistent with the DRIFTS results above. However, the IR band at 1,653 cm⁻¹ presented very weak intensity, suggesting the rapid hydrogation of monodentate formates into CH₄ during the reaction.

Similar surface information was obtained for the system operated alternatively between 10% CO₂/Ar and 40% H₂/Ar. By close examination of the MS signal of CH₄ under the transient CO₂ and H₂ conditions, it took about 1 min to fully consume the monodentate carbonates after switching from pure CO₂ to H₂, suggesting that the timescale of the reaction between surface monodentate carbonates and dissociated H is at seconds. However, in the absence of CO₂, it is quite difficulty to identify the IR band associated with the surface monodentate formates (at 1,653 cm⁻¹), confirming a comparatively fast transformation (hydrogenation) of surface formates into CHₓ.

FIGURE 8  In situ DRIFTS spectra of the catalysis over the 15Ni@NaA-SiC catalyst and corresponding MS signals collected at the exit of the DRIFTS cell as a function of time-on-stream during the catalytic CO₂ methanation under isothermal conditions at different temperatures of (a) 300, (b) 350, and (c) 400 °C. DRIFTS, diffuse reflectance infrared Fourier transform spectroscopy-mass spectroscopy; SiC, silicon carbide [Color figure can be viewed at wileyonlinelibrary.com]
Based on the in situ DRIFTS-MS studies above, the reaction pathway was proposed for CO₂ methanation over the Ni@NaA-SiC catalyst, which is shown in Figure 10. The reaction undergoes (a) CO₂ can be either linearly adsorbed on Na⁺ species via electrostatic interactions or as monodentate carbonates (1,566 cm⁻¹) adsorbed on extra framework aluminium and/or Ni⁰ species (which has been revealed by CO₂-temperature-programmed decomposition [TPD] in previous literature⁴³), while H₂ could be simultaneously dissociated on the surface of Ni⁰ species, (b) hydrogenation of the active monodentate carbonates with surface dissociated H to form monodentate formates (1,653 cm⁻¹) adsorbed on the surface of Ni⁰ species, (c) consecutive hydrogenation of these formate species into formaldehyde-like and...
methoxy species (not identified by in situ DRIFTS), and (d) desorption of methane from the catalyst surface. According to the findings discussed above, in the surface reactions (discarding the final desorption of CH₄), the hydrogenation of monodentate carbonates is the relatively slow step (since these species were always identified by in situ DRIFTS characterization), being the rate determining step. These results are in line with conclusions reported in previous studies.33

4 | CONCLUSIONS

Structured catalysts as promising alternatives to the conventional packed beds show the potential for intensifying catalysis. In this work, open-cell SiC foams are surface-functionalized with the uniformly dispersed NaA zeolite coating, then used for supporting Ni catalyst, that is, 15Ni@NaA-SiC, to intensify exothermic CO₂ methanation. The structured 15Ni@NaA-SiC catalyst demonstrated good catalytic performance regarding CO₂ conversions of ~82% (being comparable to the corresponding theoretical equilibrium conversion) and CH₄ selectivity of ~95% at 400°C. Kinetic study showed that the structured catalyst has a relatively low activation energy in comparison with the conventional packed bed configuration consisting of pelletized catalysts, that is, $E_A$ value of ~31 kJ mol⁻¹ for the 15Ni@NaA-SiC catalyst vs. ~84 kJ mol⁻¹ for the 15Ni@NaA catalyst (pellets), showing the improved ability of the structured catalyst for activating CO₂ methanation. Additionally, the structured 15Ni@NaA-SiC catalyst showed the excellent stability (i.e., 80 hr on stream) without evident deactivation. Comparative in situ DRIFTS-MS characterization of CO₂ methanation over the structured and conventional catalysts was performed, and the findings showed similar surface reactions with the hydrogenation of surface monodentate carbonates as the rate determining step. The developed structured SiC foam catalysts demonstrated satisfactory CO₂ conversion, especially at higher temperatures, and long-term stability in CO₂ methanation, being worthy of further development towards practical applications.

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NOTATION

5 | SYMBOLS

| Symbol | Definition |
|--------|------------|
| $\Delta H^\circ_{298K}$ | The standard enthalpy of reaction (kJ mol⁻¹) |
| $X_{CO_2}$ | CO₂ conversion (%) |
| $S_{CO_2}$ | CO selectivity |
| $F_{CH_4}$ | Molar flow rate of CH₄ in the outlet of reactor (mol s⁻¹) |
| $F_{CO_2}$ | Molar flow rate of CO₂ in the outlet of reactor (mol s⁻¹) |
| $W_{cat}$ | Mass of catalyst (g) |
| $C_{Ni}$ | Ni content in catalyst (g cat⁻¹) |
| $D_{Ni}$ | Ni dispersion in catalyst (g cat⁻¹) |
| $E_A$ | Activation energy (kJ mol⁻¹) |

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