CO2 Activation over Nanoshaped CeO2 Decorated with Nickel for Low-Temperature Methane Dry Reforming

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ABSTRACT: Dry reforming of methane (DRM) is a promising way to convert methane and carbon dioxide into H2 and CO (syngas). CeO2 nanorods, nanocubes, and nanospheres were decorated with 1−4 wt % Ni. The materials were structurally characterized using TEM and in situ XANES/EXAFS. The CO2 activation was analyzed by DFT and temperature-programmed techniques combined with MS-DRIFTS. Synthesized CeO2 morphologies expose {111} and {100} terminating facets, varying the strength of the CO2 interaction and redox properties, which influence the CO2 activation. Temperature-programmed CO2 DRIFTS analysis revealed that under hydrogen-lean conditions mono- and bidentate carbonates are hydrogenated to formate intermediates, which decompose to H2O and CO. In excess hydrogen, methane is the preferred reaction product. The CeO2 cubes favor the formation of a polydentate carbonate species, which is an inert spectator during DRM at 500 °C. Polydentate covers a considerable fraction of ceria’s surface, resulting in less-abundant surface sites for CO2 dissociation.

KEYWORDS: surface carbonates, in situ characterization, spectator species, CeO2 nanoshapes, CO2 activation

1. INTRODUCTION

In recent decades, economic growth has led to an increased demand for energy, which is the driving force for human welfare.1 The majority (>90%) of fuels and energy is produced by combusting fossil fuels, causing elevated CO2 emission,2 which has a major impact on global warming. Lately, many legislative and research efforts have been dedicated to the large-scale utilization of CO2 for the production of fuels and chemicals or enhanced biological and technological utilization.3 The main problem of CO2 utilization is that the molecule is very stable (ΔG298 K = −394 kJ/mol) and requires about 530 kJ/mol for the C=O bond to dissociate. Methane is an abundant hydrocarbon source that has an even higher greenhouse effect than CO2. One of the promising methods for large-scale methane and CO2 utilization is the dry reforming of methane (DRM, eq 1), which converts CO2 and CH4 into syngas (H2 and CO) with a H2/CO ratio of <1. The CO-rich syngas produced via DRM is suitable for the synthesis of dimethyl ether or long-chain hydrocarbons via the Fischer−Tropsch process.4

During the DRM reaction, several side reactions occur, such as methane cracking, the reverse water−gas shift (RWGS), and the Boudouard reaction (eqs 2−4). These favor carbon accumulation and catalyst deactivation and also impact the H2/CO ratio by lowering the H2 selectivity.5

Nickel is a promising metal for catalyzing the DRM because of its low cost, abundance, and high activity. The main disadvantage of Ni is its low carbon resistance,6 which strongly depends on the catalyst support and nickel ensemble size.7

CH4 + CO2 ↔ 2CO + 2H2 (ΔH298 K = +247 kJ mol−1) (1)

CH4 ↔ C + 2H2 (ΔH298 K = +75 kJ mol−1) (2)

H2 + CO2 ↔ CO + H2O (ΔH298 K = +41 kJ mol−1) (3)

2CO ↔ CO2 + C (ΔH298 K = −172 kJ mol−1) (4)

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Different threshold values for the nickel particle size are reported, above which carbon accumulation is initiated: about 5 nm for silica, 10 nm on γ-Al₂O₃, and 20 nm for CeZrO₂. The carbon accumulation on nickel is influenced by the metal–support interactions. Specifically in the case of ceria, a sufficient supply of oxygen species from the support has to be ensured to gasify the carbon precursors accumulating on the nickel surface. The oxygen mobility in ceria and consequently its carbon gasification efficiency can be adjusted by doping or nanoparticle engineering to preferentially expose certain facets, namely, {100}, {110}, and {111}. These facets are characterized by different energies of oxygen vacancy formation (1.96, 1.06, and 1.35 eV on {111}, {110}, and {100}, respectively), resulting in different reactivity and mobility of surface oxygen.

In recent years, a lot of research has focused on understanding the structure–activity relationships of nanoshaped ceria in different reactions. Over different CeO₂ nanoshapes, Li et al. observed a beneficial effect of CeO₂{100} and {110} crystal planes on activity for CO oxidation, compared to CeO₂{111}. A similar activity dependency trend was reported by Trovarelli et al. for the soot oxidation reaction. Zhang et al. studied the DRM reaction over Ni supported on CeO₂ nanorods and nanopolyhedra. They reported a higher catalytic activity and carbon accumulation resistance of nanorod-based catalysts, which they attributed to more abundant reactive oxygen species on CeO₂{100} and {110} crystal planes than on {111}.

On the basis of UV/vis, Raman, and XPS analyses, Wei et al. reported a decreasing abundance of oxygen vacancies as well as oxygen mobility in ceria in the following order: rods > octahedrons > cubes > particles. The catalytic activity for DRM over Ni/CeO₂ catalysts over the mentioned morphologies decreased in the same order. In addition, both DFT and experiments suggest that oxygen-assisted methane activation could be used to accelerate the C–H bond activation. Consequently, the ability to optimize ceria for accelerating CO₂ activation and dissociation and initiating oxygen spillover could be exploited to accelerate the DRM reaction and minimize carbon accumulation. Although ceria is known as a basic support, its basic/acidic properties can vary depending on the exposed facet. Remarkably active catalysts for the low-temperature methane dry reforming reaction are of great academic and industrial interest, which would increase the feasibility of decentralized natural gas valorization. A detailed structure-dependent understanding of CO₂ activation pathways on such highly active catalytic surfaces is important not only for avoiding carbon accumulation in DRM and improving stability but also for accelerating CO₂ reduction to value-added chemicals such as CO, CH₄, and methanol.

In this work, 1–4 wt % nickel was deposited on CeO₂ rods, cubes, and spheres, which in the DRM reaction exhibited notably different catalytic activity as well as the dynamics of carbon accumulation. Using temperature-programmed DRIFT-MS analyses complemented with DFT, we analyzed the CO₂ activation pathways in the absence and presence of hydrogen over the particularly promising 2Ni/CeO₂ nanorod catalyst.

2. MATERIAL AND METHODS

2.1. Synthesis of Catalysts. The nanorod (CeO₂–R)- and nanocube (CeO₂–C)-shaped CeO₂ was synthesized as reported by Zabiliškyi et al. In a typical synthesis, 58.8 g of NaOH (Merck, purity 99%) was dissolved in 140 mL of ultrapure water. A separate solution containing 4.9 g of Ce(NO₃)₂·6H₂O (Sigma-Aldrich, purity 99%) was dissolved in 30 mL of ultrapure water. After stirring for 15 min, 1 g of a powdered CeO₂ support was added and stirred for an additional 15 min. Afterward, a 2.5 wt % aqueous ammonia solution was added dropwise until the pH reached 7.5. The beaker was covered with Parafilm and stirred for an additional 2 h. After the latter, the pH value of the suspension was adjusted to 9 with a 25 wt % aqueous ammonia solution and stirred for an additional 15 min. The final product was filtered, dried at 100 °C overnight, and calcined at 500 °C for 4 h with a heating ramp of 5 °C/min.

The synthesized catalysts are denoted as xNi–R, xNi–C, and xNi–S for nanorods, nanocubes, and nanospheres, respectively, where x represents the nominal nickel content. The actual Ni content (analyzed using ICP-OES) equaled 1.95 (2Ni–R), 1.80 (2Ni–C), and 1.85 wt % (2Ni–S).

2.2. Characterization and Catalytic Testing. 2.2.1. Transmission Electron Microscopy. The phase composition and crystal structure of the samples were analyzed by transmission electron microscopy (TEM, JEM-2010F, Jeol Inc.) operating at 200 kV and equipped with a slow-scan CCD camera (Orius SC-1000, Gatan). The powdered samples were dispersed in EtOH and sonicated to prevent agglomeration and then transferred onto Cu-supported amorphous carbon lacy grids. Raw image data was processed with Digital Micrograph software (Gatan, Inc.), and selected-area electron diffraction data was simulated by electron microscopy software Java Version (JEEM 4.9).

2.2.2. BET Specific Surface Area and Porosity. The BET specific surface area, total pore volume, and pore size distribution were determined by N₂ physisorption at −196 °C (Micromeritics, model TriStar II 3020). Before the analysis, the samples were degassed in a flow of N₂ (purity 6.0, Linde) for 1 h at 90 °C, followed by 4 h at 300 °C. The total pore volume and pore size distribution values were calculated with the BJH (Barrett–Joyner–Halenda) method from the desorption branch of the isotherms.

2.2.3. X-ray Diffraction. The PANalytical Empyrean diffractometer using Bragg–Brentano geometry and Cu Kα1 radiation was used for the characterization of the crystalline phases. XRD patterns were
recorded in the 2θ range from 10 to 80°, with a measurement increment of 0.034° and a step time of 100 s.

2.2.4. Temperature-Programmed Analyses. The H₂-TPR and CO₂-TPD analyses were performed to (i) qualitatively and quantitatively assess the amount of removable oxygen as a function of ceria shape and (ii) qualitatively and quantitatively assess the number of CO₂ adsorption sites. Powdered samples (~60 mg) were positioned inside a U-shaped quartz reactor on a flock of quartz wool (Micromeritics Autochem 2920 apparatus). The analytical procedure is shown in Figure S1A. The temperature range of the H₂-TPR analysis (25–550 °C) was selected to cover the range of temperatures, probed by the catalytic tests (see below).

The dynamic structure of CO₂ bound to CeO₂–R and 2Ni–R was analyzed by temperature-programmed in situ DRIFTS-MS (DiffusIR cell from PIKE Technologies) on reduced and oxidized samples. Evolved gases were continuously analyzed by mass spectrometry. Three possible scenarios were analyzed: (A) CO₂ activation in the absence of hydrogen, (B) CO₂ activation with hydrogen species adsorbed on the catalyst, mimicked by formic acid (FA) as the probe molecule, and (C) CO₂ activation in excess gaseous hydrogen. See the Supporting Information and Figure S1 for more details.

2.2.5. In Situ Ni K-Edge XANES and EXAFS. The in situ Ni K-edge XANES and EXAFS spectra were measured in transmission mode on the 2Ni–R, 2Ni–C, 2Ni–S, and 4Ni–R catalysts, first at RT in air, then after reduction in a 5% H₂/N₂ stream (flow rate of 15 mL/min at 1 bar) for 60 min at 400 °C, and during the DRM reaction. For the latter, the catalyst was kept for 30 min at 400, 500, and 550 °C in a CH₄/CO₂ atmosphere (50% CH₄, 50% CO₂, flow rate 20 mL/min each).

We measured the XAS scans on different spots of the sample pellet to avoid potential measurement errors caused by radiation damage to the catalyst. The exact energy calibration was established with an absorption measurement on a 3-μm-thick Ni foil placed between the second and third ionization detectors. The absolute energy reproducibility of the measured spectra was ±0.02 eV.

The quantitative analysis of XANES and EXAFS spectra was performed with the Demeter program package in combination with FEFF6 program code for the ab initio calculation of photoelectron scattering paths. More details on XAS analyses are shown in the Supporting Information.

2.2.6. DFT Calculations. Electronic structure calculations were performed using VASP 5.4.1. The periodicity of the crystals was accounted for using the plane-wave formalism of the density functional theory with the projector augmented wave method. The energy cutoff of 500 eV was tested and found to suffice for well-converged results (<1 meV). The geometric optimizations were performed at the GGA+U level with the Perdew–Burke–Ernzerhof (PBE) functional in the single effect parameter (U=J) approximation, as proposed by Dudarev et al. The on-site Coulomb interaction of localized electrons was applied to Ce 4f orbitals only with U=J = 4.5 eV, as done for CeO₂ by Penschke and Paier. The 4.5 eV value for ceria in PBE+U had also been calculated self-consistently by Fabris et al. and used as such. The Grimme D3 correction for van der Waals interactions was employed.

For the bulk calculations, a 8×8×8 Monkhorst–Pack k mesh was used. For the p(2×2) slabs, a 2×2×1 mesh was found to suffice for well-converged results. For molecules in vacuum, a box with dimensions of 20×21×22 Å³ was used with gamma-point meshing.

Figure 1. Reaction rates for (A) CH₄ and (B) CO₂ as a function of temperature for 2Ni–R, 2Ni–C, and 2Ni–S catalysis. Lines are shown to guide the eye. (C) Carbon accumulated over 2Ni–R, 2Ni–C, and 2Ni–S catalysts during 1 h of TOS in methane cracking and the Boudouard reaction and 6 h of TOS during DRM at 500 °C. Stability test results at 500 °C showing (D) CH₄ conversion, (E) CO₂ conversion, and (F) the H₂/CO ratio versus time on stream.
Activation barriers for the diffusion of oxygen vacancies were calculated on previously relaxed structures, the tetrahedron method and crystal planes. The schematic of the CeO$_2$ cube aligned in the [100] orientation, with marked Miller indices for exposed crystal faces. The FFT was used for the identification of the zone axis, with marked crystal faces at the terraces and truncated edges. (C) CeO$_2$ cube in the [110] orientation, with the corresponding FFT and model in the same orientation. (D) HR-TEM of stepped [110] edge of the cube, composed of (111) steps, with marked crystal axes, faces, and structure model. Particle size distribution histograms with log-normal distribution curve for (E) CeO$_2$ cubes ($N = 100, \sigma = 9.7$) and (F) Ni nanoparticles ($N = 105, \sigma = 2.9$).

Figure 2. (A) TEM overview of the 2Ni–C catalyst comprising CeO$_2$ cubes decorated with Ni nanoparticles (red arrows). (B) Individual CeO$_2$ cube aligned in the [100] orientation, with marked Miller indices for exposed crystal faces. The FFT was used for the identification of the zone axis and crystal planes. The schematic of the CeO$_2$ cube in the [110] orientation, with the corresponding FFT and model in the same orientation. (D) HR-TEM of stepped [110] edge of the cube, composed of (111) steps, with marked crystal axes, faces, and structure model. Particle size distribution histograms with log-normal distribution curve for (E) CeO$_2$ cubes ($N = 100, \sigma = 9.7$) and (F) Ni nanoparticles ($N = 105, \sigma = 2.9$).

During the GGA+U relaxations, the threshold was set at 0.02 eV/Å. All geometries were confirmed to represent local minima by performing a vibrational analysis, where no imaginary frequencies were found. Standard dipole corrections on the z axis were used to describe the slabs.\cite{39,40} Spin polarization was used when required. Activation barriers for the diffusion of oxygen vacancies were calculated with the climbing-image nudged elastic band method with seven images.\cite{41,42}

The adsorption energies were calculated as $E_{\text{ads}} = E_{\text{adsorbate}} - E_{\text{slab}}$, where $E_{\text{adsorbate}}$ denotes the energy of the slab with the adsorbed adsorbate, $E_{\text{slab}}$ is the energy of the empty relaxed slab, and $E_{\text{gasous}}$ is the energy of the relaxed adsorbate in vacuum. The experimentally determined entropy of gaseous CO$_2$ is 213.8 J/(mol K).\cite{43} During the adsorption, CO$_2$ forms approximately one-third of its entropy, yielding 143 J/(mol K).\cite{44} The temperature of desorption is estimated from $\Delta G(T)_{\text{ads}} = 0$, where $G = H - TS = E_{\text{ads}} - TS + PV$.

For the CeO$_2$(111) and CeO$_2$(110) structure, 12-layer slabs (four O–Ce–O trilayers) with the bottom 6 layers fixed in their bulk positions were constructed. For CeO$_2$(100), an eight-layer slab was used with the bottom four layers fixed. However, because CeO$_2$(100) is a polar structure,\cite{45} the stable geometry was compensated for by moving half of the top oxygen atoms to the bottom of the slab, effectively making a nine-layer slab.\cite{46} For precise electronic energy calculations on previously relaxed structures, the tetrahedron method with Bloch corrections was used for smearing.\cite{47}

3. RESULTS AND DISCUSSION

3.1. Catalytic Activity. Preliminary catalytic results of the DRM reaction are presented in Figure S3. The following increasing trend in catalytic activity (based on CH$_4$ and CO$_2$ conversions) at identical nickel content was observed: Ni–S < Ni–C < Ni–R. By increasing the amount of nickel from 1 to 4 wt %, the conversion of CH$_4$ and CO$_2$ increased for all three CeO$_2$ morphologies, as did the H$_2$/CO ratio. The carbon accumulation rate increases with increasing nickel content (Figure S4A). As a result, further tests were focused on catalysts containing 2 wt % Ni.

Over the 2Ni–R catalyst, CH$_4$ and CO$_2$ rates of 15 and 30 mmol/g$_{\text{cat}}$·min were achieved at 500 °C, which were higher than over 2Ni–C (13 and 23 mmol/g$_{\text{cat}}$·min) and about 5 times higher than over 2Ni–S (3 and 7 mmol/g$_{\text{cat}}$·min) (Figure 1A,B). The reason for the low catalytic activity of 2Ni–S lies in the low accessibility of nickel sites, which was confirmed by pulse CO chemisorption experiments (Figure S5). The CH$_4$ and CO$_2$ rates over the 2Ni–R catalyst in the temperature range between 420 and 500 °C are more than an order of magnitude higher compared to values in the literature (Table S1 in the Supporting Information). It is evident that we are working with an exceptionally active catalyst.

Stability analysis at 500 °C for 100 h on stream revealed 53, 43 and 25% activity losses occurring over 2Ni–C, followed by 2Ni–S, and the lowest loss over 2Ni–R. In parallel, deactivation results in lowering of the reaction selectivity, namely, the H$_2$/CO ratio (Figure 1D–F).

3.2. Carbon Deposition. Reactivity and quantity of carbon deposited during DRM, methane cracking (pure CH$_4$ feed), and the Boudouard reaction (pure CO feed) were compared (Figure 1C).

The 2Ni–S sample exhibits the strongest resistance toward carbon accumulation (Figure 1C) in all three experiments,
which is likely connected to its low intrinsic activity. During the DRM reaction, the amount of deposited carbon was about an order of magnitude higher on $2\text{Ni}^{−}\text{C}$ (38 wt %) than on $2\text{Ni}^{−}\text{R}$ (4 wt %) and $2\text{Ni}^{−}\text{S}$ (2 wt %). However, during methane cracking, the $2\text{Ni}^{−}\text{R}$ accumulated the most carbon (52 wt %), compared to $2\text{Ni}^{−}\text{C}$ (32 wt %) and $2\text{Ni}^{−}\text{S}$ (1.4 wt %) (Figure 1C). This suggests that over the $2\text{Ni}^{−}\text{R}$ catalyst, both $\text{CH}_4$ and $\text{CO}_2$ activation are fast and kinetically balanced, which ensures efficient carbon gasification during the DRM reaction.

The TGA-TPO experiment was used to probe the reactivity of carbon originating from $\text{CO}$, $\text{CH}_4$, or a mixture of $\text{CH}_4$ and $\text{CO}_2$ (DRM) (Figure S4B). Carbon can exhibit markedly different reactivity, which differentiates it from spectator (blocking the catalytic surface and causing deactivation) and reaction intermediates. The latter are able to react with surface hydroxyl or (lattice) oxygen species, thus forming $\text{CO}_2$. Carbon from $\text{CO}$ (eq 4, black trace in Figure S4B) oxidizes at a lower temperature and is more reactive than carbon produced from methane cracking (red trace). Carbon accumulated during DRM (blue trace, Figure S4B) is the most stable, regardless of the CeO$_2$ morphology.

### 3.3. Structural Characterization

#### 3.3.1. TEM Analysis

Visualization of the $2\text{Ni}^{−}\text{C}$ catalyst (Figures 2A and S6) revealed CeO$_2$ cubes ranging from 10 to 50 nm in size (Figure 2E, mean size 27 nm), which are truncated at the edges and decorated with Ni nanoparticles with a mean size of 6 nm (Figure 2F). The CeO$_2$ cubes terminate with $\{100\}$ crystal facets, with a minor contribution of $\{110\}$ crystal facets exposed at the truncated part of the cubes (Figure 2B,C). The atomic resolution analysis of the $\{1−10\}$ facet representing the terrace sites of the truncated part of the cube revealed that it is actually a saw-like surface composed of steps which are about 2–4 atoms thick, following the $(111)$ crystal planes (Figures 2D and S6G).

Visualization of the $2\text{Ni}^{−}\text{R}$ catalyst (Figure 3 and S7) identified ceria rods measuring about 6–10 nm in diameter and 100–200 nm in length (Figure 3F, mean length 100 nm), decorated with Ni nanoparticles which measure about 6 nm in diameter (Figure 3G, mean size 6 nm). The surface
Table 1. Fraction of Ce³⁺ Attained during H₂-TPR, the Amount of CO₂ Adsorbed, Normalized per Mass or Surface Area of Catalysts, and the Fraction of Adsorbed CO₂ That Remains Adsorbed at up to 500 °C

| sample     | fraction of Ce³⁺ (%) | CO₂ consumption (mmol/g.cat) | CO₂ consumption (μmol/m²) | CO₂ remaining adsorbed at 500 °C (%) |
|------------|----------------------|-------------------------------|---------------------------|-------------------------------------|
| CeO₂−C    | 9                    | 0.14                          | 4.1 (2.5)                 | 50                                  |
| CeO₂−R    | 17                   | 0.30                          | 3.32 (2)                  | 37                                  |
| CeO₂−S    | 15                   | 0.2                           | 1.93 (1.2)                | 45                                  |
| 2Ni−C     | 10                   | 0.14                          | 4.25 (2.6)                | 68                                  |
| 2Ni−R     | 18                   | 0.28                          | 3.35 (2)                  | 47                                  |
| 2Ni−S     | 17                   | 0.24                          | 2.2 (1.3)                 | 47                                  |

*See the Supporting Information for calculation details. Values in parentheses represent the number of CO₂ molecules adsorbed per nm² of CeO₂.*
Figure 5. (A–C) DRIFT spectra of reduced 2Ni–C, 2Ni–R, and 2Ni–S catalysts after CO$_2$ adsorption at 25 °C and ramping to 500 °C in the 1200–1700 cm$^{-1}$ range. Evolution of νC−O carbonate, methoxy, and dioxymethylene stretching and νas,s C−H formate stretching during (D) CO$_2$-TPD and (E) FA-TPD in argon flow and (F) CO$_2$-TPD in 5% H$_2$/Ar flow over the reduced 2Ni–R catalyst.

Figure 6. Intensity profiles of characteristic IR bands during (A) CO$_2$-TPD, (B) FA-TPD, and (C) CO$_2$-TPD in 5% H$_2$/Ar flow for a reduced 2Ni–R sample. MS analysis of the evolved gases (bottom panels of A–C) and (D) the polydentate carbonate band intensity (1440–1420 cm$^{-1}$) after H$_2$ and O$_2$ pulses at 500 °C on a reduced 2Ni–R sample (upper panel) and simultaneous MS analysis of the evolved gases (bottom panel).
decomposition of adsorbed carbonates. This draws a parallel with a higher reducibility of CeO$_2$–R and CeO$_2$–S, compared to CeO$_2$–C.

3.3.5. Temperature-Programmed Activation (TPA) of CO$_2$

The reconstruction and desorption of surface carbonates in the absence of hydrogen on the 2Ni–R, 2Ni–C, and 2Ni–S catalysts were analyzed by temperature-programmed DRIFTS-MS (Figures 5A–C, 6A, and S13 and scenario A; Materials and Methods and the Supporting Information). Prior to the experiments, the samples were reduced in situ and flushed with argon at 500 °C for 30 min.

In the region between 1200 and 1700 cm$^{-1}$, bands characteristic of different carbonates on ceria were observed: monodentate (M), bidentate (B), polydentate (P), and hydrogen carbonate (HC).

Between 2S and 200 °C, 2Ni–S and 2Ni–R are populated with bidentate carbonate (1550–1570 cm$^{-1}$). The stretching of monodentate carbonate and hydrogen carbonate (M, HC 1590–1610 cm$^{-1}$) occurs in a similar region. On the contrary, on the 2Ni–C catalyst, bands at 1490 and 1385 cm$^{-1}$ are more pronounced compared to 2Ni–S and especially 2Ni–R, identifying a considerable population of polydentate carbonates on ceria nanocubes.

As the samples are heated to 400 and 500 °C, the (COO$^-$) stretching intensities of the B and M species decrease, whereas the intensity of bands between 1490 and 1385 cm$^{-1}$ increases. This reveals a reconstruction of M and B into polydentate carbonate (P) species on all three ceria morphologies.

On oxidized bare CeO$_2$–R and 2Ni–R catalyst, the carbonate signal is considerably less intense and less diverse compared to that of reduced counterparts (Figure S14), identifying the significance of Ce$^{3+}$ and O$_x$ (oxygen vacancy) sites for CO$_2$ adsorption and activation and more numerous adsorption modes of CO$_2$ on oxidized ceria surfaces.

During CO$_2$–TPD in argon (Figure 5D), the C–O stretching bands are observed in the region between 800 and 1100 cm$^{-1}$. Because there is negligible C–H stretching between 2800 and 3000 cm$^{-1}$, they belong to different surface carbonates.

Upon heating to 500 °C, a minor desorption of water is noticed because of sample dehydroxylation (Figure 6A, bottom panel). The monodentate carbonate (1600 cm$^{-1}$, blue trace) and bidentate carbonate (1550–1570 cm$^{-1}$, red trace) intensities decrease. On the other hand, the polydentate carbonate (1420–1440 cm$^{-1}$, dark trace) intensity increases (Figure 6A). This identifies partial decomposition of the carbonates and their desorption as CO$_2$ as well as a restructuring of M and B carbonate species into the thermally most stable species, the polydentate. Only a trace change in the C–H band intensity was detected (green trace in Figure 6A).

The CO$_2$–TPD DRIFTS-MS experiment over the oxidized 2Ni–R sample (Figure S15A) is characterized by the absence of the monodentate carbonate (1600 cm$^{-1}$) species and a less pronounced polydentate carbonate gain due to lower initial carbonate coverage (Figure S14).

For hydrogen-assisted CO$_2$ activation on the reduced 2Ni–R catalyst, two possibilities were analyzed: scenario B, where formic acid was used as a probe molecule because it contains two H atoms per one molecule of CO$_2$ (Figure 6B and S16B). The FA vapors were injected over the sample which was held in a flow of argon, followed by sample heating. In scenario C, the temperature-programmed CO$_2$ activation was performed while the 2Ni–R sample was held in a flow of H$_2$ (Figures 6C and S16C).

Scenario B: Initially at RT, the characteristic stretching C–H (2950–2700 cm$^{-1}$) coexists with the COO$^-$ carbonate stretchings, identifying the presence of bidentate and monodentate formate species (BF and MF, Figure S16).

The symmetric C–H stretch between 2878 and 2835 cm$^{-1}$ together with the asymmetric C–H stretch in the 2970–2920 cm$^{-1}$ region is characteristic of the dioxygenymethylene H$_2$COO$^*$ group. Additional proof of the existence of dioxygenymethylene H$_2$COO$^*$ species can be obtained from the C–O stretching region: the presence of characteristic bands at 910, 960, and 1100 cm$^{-1}$. During the FA-TPD DRIFTS experiment, there is an increase in the symmetric C–H stretch (2878–2835 cm$^{-1}$) compared to the asymmetric C–H stretch (2970–2920 cm$^{-1}$). Simultaneously, the C–O stretching of the H$_2$COO$^*$ increases. This reveals that two formate species are transformed to the dioxygenymethylene H$_2$COO$^*$ group as a result of the C–H bond cleavage and the transfer of H to the carbon atom with the simultaneous release of CO gas between 100 and 200 °C (Figure 6B).

Changes in the υC–H stretching and C–O stretching above 200 °C are caused by restructuring of the BF, MF, and H$_2$COO$^*$ into P and the desorption of CO, CO$_2$, and H$_2$O (the latter was found only in the case of an oxidized 2Ni–R sample, Figure S15B). At 300 °C, all formate and H$_2$COO$^*$ are decomposed and C–H bands disappear. Because formates are less thermally stable than carbonates, they decompose at lower temperatures and the population of inert polydentate carbonates stabilizes at about 300 °C in scenario B, compared to at 500 °C in scenario A.

During temperature-programmed CO$_2$ activation in a flow of H$_2$ (scenario C; Figures 5F, 6C, and S16), the intensity of C–H bands starts to increase at about 100 °C, reaches a maximum at 150 °C, and completely decays at 250 °C (green trace in Figure 6C). This is about 50 °C earlier compared to the case of scenario B (Figure 6B). This signifies the effect of excess hydrogen, which assists CO$_2$ conversion into carbonate species.

Unlike C–H stretching during FA-TPD, the C–H stretching observed in scenario C is shifted to lower wavenumbers (2830 cm$^{-1}$, Figure 5F). The combination of the symmetric C–H stretching at 2830 ± 10 cm$^{-1}$ with the CO stretching between 1100 and 1000 cm$^{-1}$ is characteristic of the O–CH$_x$ methoxy group. The carbonate species also give rise to C–O stretching in the 1100–800 cm$^{-1}$ region, but with a higher intensity at 850 cm$^{-1}$ (Figure 5D). When methoxy species are present in notable amounts, the intensity of bands at 850 are lower compared to that from 1100 to 1000 cm$^{-1}$ (Figure 5F).

In contrast to scenarios A and B (Figure 6A,B), the gain in P carbonates is much smaller and actually decreases to below the initial values. In excess H$_2$, the decomposition pathway of MF and BF is shifted away from P and steered toward methane and water (green trace, bottom panel of Figure 6C), apparently through the formate and methoxy intermediates (together with the disappearance of C–H and C–O stretching, Figure 5F). Under hydrogen-lean conditions, formate and H$_2$COO$^*$ decompose to CO.

Pulse CO$_2$ isothermal experiments at 500 °C (Supporting Information, Figure S17) in the presence of hydrogen increase CO formation and correlate well with the temperature-programmed experiments described above (scenarios A–C).

3.3.6. Probing Carbonate Reactivity with H$_2$ and O$_2$

Pulse Experiments. Reduced 2Ni–R was pretreated with CO$_2$ at 500 °C (Figure S1B) to populate its surface with polydentate

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carbonates, H₂ pulses were injected at the same temperature, and DRIFTS-MS was used to analyze the catalyst surface and evolved gases. During the H₂ pulses, no decrease in the polydentate signal was observed (Figure 6D). Consequently, in the transient experiment, H₂ is inefficient in reacting with the polydentate carbonate at a kinetically relevant rate. Therefore, it is reasonable to assume that they mainly act as spectators during the DRM reaction. The MS signal for water (m/z = 18) and the trace signal for CO were observed during H₂ pulsing (bottom panel of Figure 6D). This suggests that H₂ preferably reacts with lattice oxygen, causing catalyst reduction as well as removing the remaining M and B carbonates.

Contrary to hydrogen, oxygen pulses at 500 °C caused a noticeable drop in the polydentate band intensity (Figure 6D). Catalyst oxidation caused the destabilization and desorption of surface carbonates as CO₂ and trace amounts of CO (bottom panel in Figure 6D). This is consistent with (a) a much lower density of surface carbonates on oxidized compared to partially reduced ceria surfaces (Figure S14) and (b) DFT calculations reported in section 3.3.7.

3.3.7. In Situ Ni K-Edge XANES and EXAFS Analysis. At RT in air, nickel is present exclusively as Ni²⁺ on all three CeO₂ morphologies (Figures 7 and S18–S25). After activation in a 5% H₂/N₂ flow, between 60 and 70% of the Ni²⁺ is reduced to metallic Ni (Ni⁰). This fraction of Ni⁰ is retained during the DRM reaction at 400 °C.

During the DRM reaction at 500 °C, the fraction of Ni⁰ increased to 85, 85, and 90% in 2Ni–C, 2Ni–S, and 2Ni–R, respectively. At 550 °C, the fraction of Ni⁰ exceeds 90% in all catalysts. A very similar trend in the temperature-dependent evolution of the nickel oxidation state was also observed for the 4Ni–R catalyst (Figure S22).

In situ Ni K-edge EXAFS analysis was used to monitor the changes in the local structure around nickel under the above-mentioned conditions. In all studied catalysts in air at RT, Ni²⁺ is coordinated with oxygen atoms in the first coordination shell and with Ni and O in more distant coordination shells at distances characteristic of NiO (Figures S26–S29). In the 2Ni–R sample, the coordination numbers are significantly lower than in the bulk NiO (Tables S3–S5), indicating that nickel is in the form of small clusters, measuring below 1 nm in diameter. The estimated size of NiO clusters does not change when the nickel content is increased from 2 to 4 wt%: their structural parameters are the same (Table S5). In the 2Ni–C catalyst, the size of NiO nanoparticles is estimated to be about 2 nm.

In the case of 2Ni–S, the NiO nanoparticle size, estimated from the average coordination number, is smaller compared to those in the 2Ni–R sample. All Ni²⁺ cations are connected to Ce atoms (forming Ni–O–Ce bridges), indicating that nickel is in the form of two-dimensional thin islands, coating the CeO₂ surface.

EXAFS is a bulk analysis method and is not as localized as TEM visualization. The variation in the NiO particle size, estimated by TEM and EXAFS, likely originated from the polydisperse size distribution of NiO in the catalysts. The NiO crystallites measuring about 6–10 nm (visualized by TEM) coexist with the subnanometer NiO clusters, which are the majority phase (detected by EXAFS).

During catalyst activation at 400 °C, the nearest-neighbor Ni–Ni distances are the same as in Ni metal fcc (2.48 and 3.52 Å). More distant Ni neighbors expected in the Ni fcc metal structure are below the limit of detection, indicating that the average size of Ni metal clusters is below 1 nm. A portion of Ni cations remain in the Ni²⁺ state, as demonstrated by the XANES analysis, and the local structure remains the same as in the NiO crystal (Ni–O and Ni–Ni distances are the same as in the NiO crystal: 2.07 and 2.97 Å, respectively). During the DRM reaction at 400 °C, there are no significant structural changes in the Ni metal or NiO clusters (Tables S6–S9).

During the DRM reaction at 500 and 550 °C, some changes in the local Ni structure are observed among the three CeO₂ morphologies. In the case of 2Ni–R, the Ni–Ni coordination number of the metallic species becomes higher than that in 2Ni–C. The lowest Ni–Ni coordination remains in 2Ni–S. This reveals that under the DRM conditions at 500 and 550 °C the restructuring of the nickel phase is most prominent on ceria nanorods. Mao and Campbell reported that an oxophilic
metal such as nickel is repelled by surface oxygen vacancy sites of ceria and that nickel prefers to be associated with surface oxygen atoms. The most extensive reduction of the 2Ni–R catalyst (Table 1) results in fewer surface oxygen sites, where nickel is preferably aggregated, favoring nickel coalescence and the formation of larger Ni clusters. Over ceria nanocubes, the fraction of Ce⁴⁺ is lower, resulting in a higher abundance of oxygen sites which bind nickel more strongly. Also, the jagged surface of ceria nanocubes (Figure 2D) makes the diffusion of nickel across the step sites energetically much more demanding compared to the diffusion over extended closely packed (111) terraces. Furthermore, if single atom nickel atoms were present in substantial amounts, then the Ni–O–Ce chemical bonds would be discovered during EXAFS fitting. This was not the case.

3.3.8. DFT Calculations. On the basis of TEM characterization, {111} and {100} are the most abundant terminating facets on the synthesized CeO₂ materials. We include the {110} facets in our calculations, which are also commonly exposed. ¹,²,¹³,⁶³,⁶⁶

3.3.8.1. CeO₂(111). For {111}, the stoichiometric surface will be stable under high oxygen pressures. ⁶⁷ Under lower pressures, the surface gets progressively reduced. ⁶⁸ It has been shown that vacancies form in the first subsurface layer and do not agglomerate. ⁶⁹ In the oxygen-lean limit, all subsurface oxygen atoms are removed and the ensuing structure undergoes a reconstruction with a change in the stacking of the surface Ce and O layers, gaining 0.3 eV.⁷⁰

We investigate the stoichiometric surface (CeO₂(111)), the surface with 0.25 ML of subsurface vacancies (CeO₂(111)(1/4ss)), and the surface with 1.00 ML of subsurface vacancies and the stacking fault (CeO₂(111)(111)₁₁₁(1ss+stacking)).

When oxygen is removed from the surface, a surface vacancy is first created (CeO₂(111)(111)₁₁₁(1ss)). Overcoming a small barrier of 0.27 eV, the subsurface oxygen migrates to the surface, forming CeO₂(111)(111)₁₁₁(1ss+stacking), which is 0.28 eV more stable. However, the vacancies in the subsurface are mobile (Eₐ = 2.81 eV for diffusion), and the least stable surface vacancies can diffuse at high temperature (Eₐ = 1.94 eV for diffusion). This explains why vacancies do not agglomerate.⁶⁹

A fully reduced surface CeO₂(111)₁₁₁(1ss+stacking) restructures to CeO₂(111)₁₁₁(1ss+stacking) upon overcoming a barrier of 1.05 eV, lowering its energy for 0.38 eV. This is in agreement with the findings from Lustemberg et al.⁷⁰ All structures are shown in Figure S29.

3.3.8.2. CeO₂(110). On stoichiometric CeO₂(110), oxygen vacancies can also form on the surface and in the subsurface.⁷¹ A surface oxygen vacancy is thermodynamically 0.85 eV more stable than a subsurface one. Subsurface vacancies are also kinetically unstable, requiring only 0.04 eV to migrate to the surface. Diffusion of the oxygen vacancies on the surface can happen along (Eₐ = 1.76 eV) or across (Eₐ = 0.92 eV) the Ce–Ce rows. Thus, we will limit our calculations to the stoichiometric surface and surface vacancies. All structures are shown in Figure S29.

3.3.8.3. CeO₂(100). Because of the polarity of the CeO₂(100) surface, half of the surface oxygen atoms must be displaced to the bottom of the slab (Model B0 from ref 4). Adding an additional formula unit of CeO₂ to the surface yields Model C0, which is slightly more stable. We will analyze both terminations because of their almost identical surface energies (γ₁₀₀ = 0.102 eV Å⁻², γ_3₀ = 0.105 eV Å⁻²).⁷² For the B0 surface, we investigate the structure with one surface oxygen vacancy (B₁ᵥ) and with one subsurface oxygen vacancy (B₁ᵤ). For the C0 surface, two surface oxygen vacancies (C2) are considered.

On B0, a surface oxygen vacancy is slightly (0.14 eV) more stable than a subsurface one. The barrier for its migration in the subsurface is also low (Eₐ = 0.23 eV). Hence, both structures can exist under oxygen-lean experimental conditions. In the subsurface, there are two unequivocal sites for oxygen vacancies: below the surface oxygen atoms (structure B₁ᵥ) and below the Ce–Ce bridge position, with the latter being much less stable (+1.33 eV). Consequently, diffusion in the subsurface is not likely (Eₐ = 1.37 eV), whereas it proceeds readily on the surface (Eₐ = 0.63 eV). Figure S30 shows all five mentioned surface structures of ceria.

3.3.8.4. CO₂ Adsorption on CeO₂(111) Surfaces. CO₂–TPD clearly shows three types of adsorbed CO₂ on the partially reduced CeO₂ surfaces (Figures S8 and S12), which are assigned to the monodentate (M), bidentate (B), and polydentate (P) species. This is in excellent agreement with the DFT data for the (111) surface at all levels of oxidation (CeO₂(111), CeO₂(111)(1/4ss), and CeO₂(111)(1ss+stacking)).

When CO₂ is planarly positioned above the surface, the geometric and electronic structures are not perturbed noticeably and a very weak interaction of ~0.15 eV (irrespective of the surface) results, which is merely physisorption.

CO₂ can bind in a monodentate fashion in the tilted orientation atop the Ce atom, forming an angle of 54° with the surface at a O–Ce distance of 2.96 Å. The interaction energy is ~0.24 eV on all surfaces. There is negligible charge transfer from the catalyst to CO₂, no geometric distortion of CO₂, and no perturbation in the density of states (Figure S31).

CO₂ can also adsorb in a bidentate fashion through Ce–O and O₅₆₇₈–C with physisorption (~0.38, ~0.28, and ~0.33 eV on CeO₂(111), CeO₂(111)(1/4ss), and CeO₂(111)(1ss+stacking)), thus effectively forming a carbonate species with one free (dangling) oxygen. In CO₂, the O–C–O angle is distorted from 180 to 131° and the O–C bonds are elongated to 1.29 and 1.22 Å. The Ce–O bond length is 2.38 Å, and the O₅₆₇₈–C bond length is 1.43 Å. There is some charge transfer as the CeO₂(111) surface donates 0.15e⁻ to CO₂, the CeO₂(111)(1/4ss) surface donates 0.21e⁻, and the CeO₂(111)(1ss+stacking) surface donates 0.27e⁻.

The strongest interaction of CO₂ with CeO₂(111) occurs when it adsorbs as a polydentate/tridentate species (~0.68, ~0.71, and ~0.70 eV on CeO₂(111), CeO₂(111)(1/4ss), and CeO₂(111)(1ss+stacking)), respectively, forming one Ce–O and two O₅₆₇₈–C interactions. The resulting carbonate species has the original C–O bonds elongated to 1.27 Å and the O–C–O angle is further decreased to 129°. The Ce–O bond lengths are 2.54 Å and the O₅₆₇₈–C bond length is 1.38 Å. The charge transfer is 0.17 e⁻ from CeO₂(111) and 0.27 e⁻ from CeO₂(111)(1ss+stacking). As shown in Figure S31, the electronic density of the surface is not noticeably perturbed by the adsorbed CO₂ molecule. The three adsorption modes are shown in Figure 8. The adsorption interaction and charge transfer slightly increase as the surface gets reduced.

We estimate the approximate temperatures, where differently bound CO₂ is released, setting ΔG(T_ads) = 0. The monodentate species would desorb from CeO₂(111) at 99 °C, the bidentate species at around 316 °C, and the polydentate/tridentate/carbonate species at 781 °C. On the reduced surfaces, these values are comparable. Note that the values are strongly dependent on the accuracy of DFT data and can easily
First, we treat B0 and B1\textsubscript{n} structures concomitantly because they differ only in one subsurface oxygen and feature the same adsorption modes. When CO\textsubscript{2} is planarly above the surface Ce atom, the purely physisorption interaction is weak (−0.07 eV). When CO\textsubscript{2} binds as a monodentate species, it sits in the bridge position of the removed surface oxygen atom, forming an angle of 37.4° with the surface at a O–Ce distance of 2.76 Å. The geometry of the molecule is not distorted, and there is no charge transfer. The adsorption interaction is −0.49 eV.

Somewhat surprisingly, the bidentate mode of adsorption is weaker (−0.38 and −0.09 eV for B0 and B1\textsubscript{n} respectively). Here, upon the formation of the Ce–O and O\textsubscript{surf}–C bonds, CO\textsubscript{2} is adsorbed as a carbonate species with one free (dangling) oxygen. The O–C–O angle is reduced to 131 °C, and the O–C bonds are elongated to 1.31 Å (toward C(−O\textsubscript{surf})) and 1.21 Å (toward the dangling oxygen). CO\textsubscript{2} interacts most strongly with Ce\textsubscript{O\textsubscript{2}}(100) when it binds as a tridentate species with one Ce–O and two O\textsubscript{surf}–C interactions. Incorporating into the lattice horizontally, the adsorption energies are −2.45 and −1.66 eV on B0 and B1\textsubscript{n}, respectively. A proper carbonate species with three equally long C–O bonds (1.30 Å) is formed. There is a considerable charge transfer from the surface to the CO\textsubscript{2} molecule (−0.27\textsubscript{e\textsubscript{g}}), and the entire carbonate molecule is negatively charged (−1.33\textsubscript{e\textsubscript{g}}). Experimentally, two distinct adsorption modes can be observed: the monodentate and the carbonate species. However, under oxygen-lean conditions there will be surface oxygen vacancies present, which introduces additional possibilities, as shown below.

On the B1\textsubscript{n} surfaces, more adsorption modes are accessible because of the available oxygen vacancy. Again, CO\textsubscript{2} can interact planarily (−0.07 eV), as a monodentate species (−0.60 eV), as a bidentate species (−0.91 eV), or as a carbonate species (−3.28 eV). The two additional adsorption modes of CO\textsubscript{2} include a bent geometry: the carbon atom can occupy the hollow (−0.57 eV) or the bridge surface site (−0.87 eV), with the CO\textsubscript{2} molecule positioned horizontally.

C0 and C2 exhibit similar adsorption modes of CO\textsubscript{2}. When located horizontally above the surface Ce atom, the CO\textsubscript{2} interaction is negligible (−0.02 eV). It can also adsorb as a monodentate species atop the Ce (−0.21 eV) without noticeable geometry distortion, electronic perturbation, or charge transfer. On C2, a bridge position for the monodentate species is also possible (−0.51 eV), while on C0 the bridge position is not particularly stable (−0.16 eV). CO\textsubscript{2} can be positioned between the adjacent Ce adatoms (−0.53 and −0.36 eV on C0 and C2, respectively). On C0, there are two distinct, equally strong adsorption modes. CO\textsubscript{2} can bind as a bidentate (Ce–O and O\textsubscript{surf}–C) or a carbonate (Ce–O and two O\textsubscript{surf}–C) species, with both exhibiting an adsorption energy of −1.09 eV. On C2, the carbonate species is bound similarly strongly (−0.91 eV). However, because of two missing surface oxygen atoms, there is a particularly strong (−1.96 eV) adsorption mode with CO\textsubscript{2} incorporating into the lattice on the surface. All adsorption modes are shown in Figure 9.

3.3.8.7. CO\textsubscript{2} Adsorption on the Ni(111) Surface. The adsorption of CO\textsubscript{2} on nickel has already been thoroughly researched by Wang et al.\textsuperscript{22} Using the GGA level of DFT, adsorption energies on Ni(111), Ni(110), and Ni(100) were calculated. The authors found that on Ni(111), which is the most stable and common nickel surface, CO\textsubscript{2} can adsorb in four different ways with similar interactions (0.31–0.46 eV).

Figure 8. Adsorption modes of CO\textsubscript{2} on Ce\textsubscript{O\textsubscript{2}}(111), Ce\textsubscript{O\textsubscript{2}}(111)(1/4ss), Ce\textsubscript{O\textsubscript{2}}(111)(1ss+stacking), Ce\textsubscript{O\textsubscript{2}}(110), and Ce\textsubscript{O\textsubscript{2}}(110)(11). The values represent adsorption energies in eV.

Figure 9.
Our results confirmed these and found that the adsorption energy of the lowest-lying intermediate is 0.53 eV, which is in reasonable agreement with the data from Wang et al. In the most favorable configuration (4-5fcc), CO$_2$ assumes a bent geometry with a O−C−O angle of 132°. The carbon atom is positioned between the fcc and bridge sites, and the oxygen atoms interact with two neighboring Ni atoms (\(d(\text{Ni}−\text{O}) = 2.11\) Å). The other adsorption modes are similar in energy (0.3−0.5 eV). See Figure S32 and Table S10 for geometries and energies.

Although we studied the adsorption of CO$_2$ and the formation of different surface motifs, the decomposition of CO$_2$ into CO has been studied elsewhere. Because of a strong repulsion between the surface oxygen atoms and the newly formed O*, this is feasible on oxygen-deficient surfaces. Kildgaard et al. studied this reaction on CeO$_2$−x(111) and found that carbonate cannot decompose to CO because of a barrier of 2.6 eV. Hence, a secondary metal (Ni) is required.\(^7\)

4. DISCUSSION

Chemically identical catalysts, all containing 2 wt % nickel on ceria rods, cubes, and spheres exposing predominantly (111) and (100) facets, provide very different activity, stability, and carbon accumulation resistance in the low-temperature DRM reaction. We established the following decreasing trend in catalytic activity: 2Ni−R > 2Ni−C > 2Ni−S. The initial size of the nickel clusters, estimated via \(\text{in situ}\) EXAFS analysis, was found to be very similar on all ceria shapes (~1 to 2 nm), as was the fraction of metallic nickel which reaches 90–95% at 550 °C during the DRM reaction.

A strong inverse correlation exists between the carbon accumulated during the DRM reaction and the fraction of Ce$^{3+}$ quantified during H$_2$-TPR analysis. The facile reduction of the 2Ni−R catalyst terminated predominantly with the (111) facet.

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**Figure 9.** Adsorption modes of CO$_2$ on CeO$_2$(100):B0, CeO$_2$(100):B1ss, CeO$_2$(100):B1s, CeO$_2$(100):B2s, CeO$_2$(100):C0, and CeO$_2$(100):C2s. Adsorption values are in eV.

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ensures efficient carbon gasification during DRM with mobile oxygen species originating from CO$_2$.\textsuperscript{7,54}

The lowest catalytic activity and carbon deposition on 2Ni–S are due to the partial inaccessibility of Ni active sites to gaseous reactants, caused by the close packing of ceria crystallites.

The catalyst deactivation strongly depending on the surface morphology of nanoshaped ceria is most extensive over 2Ni–C terminated with the (100) facet. During methane cracking in the absence of oxidant, the highly active 2Ni–R sample was most extensively coked. However, the 2Ni–C accumulated by about an order of magnitude more carbon during DRM compared to two other tested catalysts.

The following phenomena likely contribute to extensive coking and deactivation over 2Ni–C: (i) the redox chemistry of ceria cubes is least prominent, leading to lagging oxygen supply to the nickel, resulting in slow carbon removal, and (ii) the surface of cubes during the DRM reaction is most densely populated with stable polydentate carbonate spectator species, which additionally hinders oxygen mobility and the participation of oxygen species in the catalytic cycle.

Our DFT calculations reveal a much stronger adsorption interaction of the carbonate species on stoichiometric CeO$_2$(100) (2.45 eV) than on CeO$_2$(111) (0.7 eV) or CeO$_2$(110) (1.53 eV).

Moreover, both DFT and CO$_2$-TPD analyses show that oxygen-deficient (100) facets provide stronger binding sites compared to (111).

According to experimental data shown in Table 1, 2.0–2.6 CO$_2$ molecules bind per nm$^2$ of CeO$_2$ (rod and cube morphology, respectively) and 1.2–1.3 bind per nm$^2$ in CeO$_2$ spheres, which is due to the close packing of individual ceria crystals and the poor accessibility of its surface.

The interaction between Ni(111) and CO$_2$ has been computed to be roughly 0.5 eV, whereas on various CeO$_2$–x surfaces this interaction can exceed 1.0 eV for polydentate species.

Consequently, CO$_2$ predominantly adsorbs and undergoes activation on CeO$_2$–x and not nickel. This is further confirmed by the similarity of DRIFT spectra of pure ceria supports and Ni–CeO$_2$ catalysts as well as the difference spectra at 500 °C (Figures S13 and S33).

For the sake of completeness, we also analyzed a 2 wt % Ni/SiO$_2$ sample under identical conditions as for Ni/CeO$_2$–R for the carbonate population (Figure S34). We can see a much lower (negligible) carbonate signal on Ni/SiO$_2$. This indicates a fundamentally different chemistry of both materials (Ni/SiO$_2$ and Ni/CeO$_2$) for CO$_2$ activation and adsorption.\textsuperscript{75}

The function of nickel is methane activation and the supply of hydrogen species via spillover to facilitate the reaction of different surface carbonates (excluding polydentate).

The following arguments regarding the reactivity of different carbonates, populating fully oxidized or partially reduced (111) ceria nanorod surfaces, can be put forward.

On the basis of the temperature-programmed DRIFTS-MS experiments, a mechanism of CO$_2$ activation on a partially reduced ceria surface in the absence or presence of hydrogen is proposed (Figure 10).

CO$_2$ adsorbs on a bare CeO$_2$–x surface as M, B, and P carbonate species (only M and B are shown for clarity). Upon heating in the absence of hydrogen (red arrow, position 2), the M and B carbonates rearrange into the P carbonate or desorb as CO (minor pathway) or CO$_2$ (major pathway).

In the presence of H species, bidentate and monodentate formate are formed (blue-green arrow, position 3). The hydrogenation of B carbonate to BF is shown above the blue-green arrow. With increasing temperature, two possibilities exist: (i) Under hydrogen-lean conditions (green arrows), the formates partially decompose to CO and CO$_2$ and partially rearrange and hydrogenate into H$_2$COO$_2$ intermediates (via hydrogen produced during formate decomposition, highlighted by the blue dashed arrow, position 4). The H$_2$COO$_2$ group (position 4) can then further decompose to CO and H$_2$O by weakening of the C–O bond in the carbonate species, arriving...
at position 7. (ii) In excess hydrogen, (blue arrows, where H* represents adsorbed hydrogen species which are present in excess), the formate readily converts to H₂COO* and further to methoxy groups (attached via an oxygen atom to the cerium atom, positions 5 and 6). The methoxy can further hydrogenate to CH₃ with byproducts of CO and H₂O. This is supported by a DRIFTS-MS experiment, where a simultaneous decrease in bands characteristic of C=O and C–H stretching takes place together with the identification of methane gas. In parallel, MP and BF can also desorb as CO₂
and H₂O or convert to P carbonates (positions 4, 6, and 7). To further substantiate the conversion of methoxy to methane, Wang et al.²⁹ observed that the hydrogenation of methanol to methane occurs easily over the Ru/CeO₂ catalyst at 300 °C. Also, Kawi et al.²⁷ observed that formate and methoxy species are important intermediates during CO₂ hydrogenation to methane over Ni/ CeO₂ catalysts.

No decrease in the polydentate band intensity was detected during the injection of H₂ pulses over the 2Ni–Ru catalyst at 500 °C (Figure 6D). This is in line with our experimental and DFT analyses of the polydentate carbonate binding strength on partially reduced ceria and likely also acts as a spectator during the DRM reaction. As a result, only a minor fraction of the ceria surface remains vacant to facilitate the dissociative CO₂ activation at 500 °C (Table 1). The presence of hydrogen favors the transformation of monodentate and bidentate to CO, thus partially preventing their conversion to polydentate carbonate (Figures 6C and S16).

5. CONCLUSIONS

Nickel crystallites measuring about 1 nm in size were dispersed on ceria nanorods which predominantly expose {111} crystal facets. This produced an exceptionally active and stable DRM catalyst with low carbon accumulation, compared to ceria nanocube and nanosphere morphologies. This can be attributed to the synergetic actions of highly dispersed nickel for methane activation and the intermediate CO₂ binding strength of the CeO₂ nanorod surface for the stabilization of reactive M and B carbonates as well as high reducibility for facile CO₂ dissociation. Catalytic stability is influenced by the terminating ceria facets: the jagged (100) surface present in ceria nanocubes helps maintain the structural integrity of nickel by preventing its sintering but causes severe coking due to poor redox activity.

CO₂ adsors on (sub)stoichiometric ceria surfaces as monodentate, bidentate, and hydrogen carbonate species at room temperature. The polydentate carbonate population is favored over the {100} facet of ceria, which prevails in the ceria nanocube surface. On the contrary, monodentate and bidentate carbonates prevail on the {111} facet. The monodentate or bidentate species and the polydentate species on fully oxidized CeO₂(111) are bound more weakly than on CeO₂(100). The oxygen-deficient (partially reduced) ceria surfaces provide the strongest interaction with CO₂ especially CeO₂(100).

The most thermally stable polydentate (P) carbonate which covers a large fraction of the partially reduced ceria surface reacts sluggishly with H₂ revealing P to be a spectator rather than an active species during the DRM reaction at 500 °C. The presence of hydrogen increases the reactivity of the surface carbonates and partially prevents their restructuring to inert polydentate, supporting the hydrogen-assisted CO₂ activation pathway on Ni/ CeO₂[100]. In a surplus of hydrogen, the dioxydimethylene converts to methane and water via methoxy, whereas under H₂-lean conditions, dioxydimethylene preferentially decomposes to CO and water.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.2c05221.

Additional explanations, kinetic analysis, catalytic performance comparison, carbon accumulation analysis, CO chemisorption, HR-TEM and SAED images, N₂ physisorption data, XRD results, H₂-TPR profiles, CO₂ DRIFT spectra and temperature-dependent desorption profiles, XANES and EXAFS spectra and fitting results, ceria surface models, and DFT-calculated CO₂ adsorption parameters (PDF)

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Notes
The authors declare no competing financial interest.

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