Development of Highly Stable Low Ni Content Catalyst for Dry Reforming of CH₄-Rich Feedstocks

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Highly active and coking-resistant Ni catalysts suited for the dry reforming of CH₄-rich gases (70 vol.%, e.g., biogas or sour natural gas) were prepared starting from a Mg-rich Mg–Al hydrotalcite support precursor. Calcination at 1000°C yields two phases, MgO and MgAl₂O₄ spinel. Complexation-deposition of Ni with citric acid on the preformed support as well as lanthanum addition yields a catalyst with remarkably low carbon accumulation over 100 h on stream attributed to both high Ni dispersion and preferred interactions of Ni with MgO on MgAl₂O₄.

Global energy demand is rapidly growing, and over 80% thereof is covered by fossil fuels in recent times.[11] Natural gas and biogas are emerging feedstocks for the energy market due to their abundance and low specific carbon footprint of the main component methane.[2-4] However, most natural gases and biogases contain varying amounts of other compounds.[5] For instance, some major natural gas sources in Vietnam[6] or biogas in Germany[7] contain a high fraction of CO₂ (~30 vol.%). As separation is costly, dry reforming (DRM) is considered to directly convert such CO₂-rich gases into synthesis gas, a highly preferred starting material in large-scale chemical syntheses.[8] Mostly, DRM has been investigated with stoichiometric mixtures of CH₄ and CO₂. Processing feeds with an under-stoichiometric concentration of CO₂ via DRM may lead to higher H₂ fractions but encounters high coking rate due to the shortage in CO₂, which otherwise removes the surface carbon via gasification during the reaction.[9]

Nickel is the most commonly studied non-noble metal in DRM[10] because of its low cost and high availability.[11] However, Ni catalysts are prone to fast deactivation by coke deposition.

Consequently, this issue was tackled via applying basic supports, adding dopants/modifiers, controlling the metal loading, or tuning preparation methods and thermal pretreatment.[5,10] Another serious problem is the aggregation of Ni species to larger but less active particles.

Several main steps rule the DRM reaction:[11] (1) Dissociative adsorption of CH₄ and CO₂, (2) first desorption of CO and H₂, and (3) formation of surface hydroxyls and oxygen spill-over and (4) surface hydroxyls and oxygen oxidize CH₄ species and second desorption of CO and H₂. The adsorbed oxygen species from CO₂ dissociation react with carbonaceous intermediates (Table S.1) which otherwise would form carbon. Consequently, we chose several approaches to enhance the activation of CO₂ at high Ni metal dispersion to suppress methane decomposition.

In our previous study on stoichiometric DRM (CH₄/CO₂ = 1), MgO–Al₂O₃ supported Ni catalyst modified with La and citric acid (CA) (denoted as LaNi(CA)/Mgₓ₁₋₁AlₓO₄) turned out to be most effective.[11] However, the coking behavior of this sample in CH₄-rich DRM is still unsatisfactory and limits process development. In this study, the thermal pre-treatment of the Mg-rich Mg–Al hydrotalcite support precursor was extended from 550 to 1000°C. With this modification, the nature of the support was significantly changed as disordered oxide phases were formed, leading to improved interactions with the subsequently added Ni during DRM. The scheme of the preparation route is shown in Figure S.1. For comparison, two catalysts were prepared on supports which were initially treated at 550°C. Pathways for carbon formation were studied in order to understand the relationship between catalyst properties and coking resistance.

XRD pattern of the support Mgₓ₁₋₁AlₓO₄•1000 (prepared by pre-treating Mgₓ₁₋₁AlₓO₄ at 1000°C) shows sharp reflections of periclase (the cubic form of MgO, ICDD file No. 01-071-1176)[13] and MgAl₂O₄ (ICDD file No. 00-021-1152)[14] crystalline phases (Figure 1a). The corresponding catalysts Ni/Mgₓ₁₋₁AlₓO₄•1000 and LaNi(CA)/Mgₓ₁₋₁AlₓO₄•1000 display patterns close to that of the support, suggesting the formation of finely dispersed La⁺⁺ and Ni⁺⁺ species that are not detectable by XRD.[15] Moreover, magnification of the pattern for LaNi(CA)/Mgₓ₁₋₁AlₓO₄•1000 in the 20 range from 61° to 64° exposes a slight shift of the reflection at 62.3° to higher 20 values compared to support (Figure S.2). This shifts suggest the presence of NiO–MgO solid solution in LaNi(CA)/Mgₓ₁₋₁AlₓO₄•1000 formed from the Ni precursor and the preformed small MgO particles of 8–9 nm crystallite size.[16] In contrast, in Mgₓ₁₋₁AlₓO₄ and corresponding catalysts the crystalline MgO (periclase) did not form. Instead, existence of

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MgO–Al₂O₃ solid solution is suggested which was previously discussed. [12]

Regarding the chemical surface states, the Ni 2pₓᵧ binding energy (Figure S. 3) from the XPS measurement of Ni/Mg₁.₃ Al₂O₃ (856.9 eV) indicates Ni²⁺ located at the surface as NiAl₃O₄ spinel (856.8 eV). [17] The Ni 2pₓᵧ binding energy of Ni/Mg₁.₃ Al₂O₃, 1000 (856.1 eV) is close to that of Ni surface species in NiO–MgO solutions (855.7–856.0 eV). [18–19] However, no Ni 2pₓᵧ signal was found in Ni/MgO with same Ni load, probably due to the migration of NiO into bulk MgO at high calcination temperature. [20] This confirms the unique structure of Mg₁.₃ Al₂O₃, 1000, which can stabilize Ni in NiO–MgO solid solution but still offers surface Ni species that are beneficial for the catalytic activity.

Compared to pure NiO which can be significantly reduced at 400 °C, [12] all supported Ni samples display poorer reducibility in H₂-TPR experiments (Figure 1b) as the main reduction peaks appear first above 600 °C (β and γ peaks). This behavior is assumed to be caused by the strong metal-support interactions (MSI) at low Ni loading allowing Ni²⁺ to disperse easily into stable structures. [21–22] Ni/Mg₁.₃ Al₂O₃, 1000 discloses poorer overall reducibility compared to Ni/Mg₂ Al₂O₃, illustrated by a higher percentage of H₂ uptake in γ peak (Table S. 2) and lower total H₂ consumption (Table 1).

LaNi(CA)/Mg₁.₃ Al₂O₃, 1000 consumes less H₂ in TPR than LaNi(CA)/Mg₂ Al₂O₃ but more than Ni/Mg₁.₃ Al₂O₃, 1000 (Table 1) and even more than the theoretical value for complete Ni²⁺ reduction (428 µmol). The latter can be traced back to enhanced oxygen activation from distorted Ni surface structures that will be discussed below in the UV-Vis section. Besides, it should be noted that CA-assisted preparation increases the Ni²⁺ dispersion. [21] However, similar to LaNi(CA)/Mg₁.₃ Al₂O₃ sample LaNi(CA)/Mg₂ Al₂O₃, 1000 exposes a reduction peak below 600 °C (α peak) but with higher intensity (Figure 1b, Table S. 2). This effect is attributed to the presence of La that promotes the oxygen mobility and/or formation of defect structures where MgO is doped with Ni²⁺. [12,24] On the other side, sample LaNi(CA)/Mg₁.₃ Al₂O₃, 1000 exposes the β peak at a temperature similar to that of LaNi(CA)/Mg₂ Al₂O₃ and an additional split γ peak at very high temperature (980 °C) assigned to Ni in strong interaction with the support. [21]

These β and γ Ni²⁺ species are poorly reduced in usual pretreatment and therefore LaNi(CA)/Mg₁.₃ Al₂O₃, 1000 is only partially reduced before DRM. The Ni metal fraction after in situ reduction was evaluated in a two-step experiment: first, the reduction at 700 °C was made, directly followed by a regular TPR experiment up to 1000 °C. This revealed a H₂ uptake of 292 µmol/g, corresponding to 59% of the value for the fresh
catalyst at 700 °C. The rest is still Ni^{2+} (Figure S. 4). This means that a large fraction of the Ni is in oxidised state after reduction.

Compared to support, Ni/Mg\textsubscript{1.3}AlO\textsubscript{x} has similar BET surface area, whereas that of LaNi(CA)/Mg\textsubscript{1.3}AlO\textsubscript{x} is lower, probably caused by La addition (Table 1). The Mg\textsubscript{1.3}AlO\textsubscript{1000} supported catalysts expose significantly lower values compared to Mg\textsubscript{1.3}AlO\textsubscript{x}-based materials, whereas La addition has no significant influence in this case.

The UV-Vis DR spectra in the region of 200–350 nm (Figure S. 5) give hints on the Ni^{2+} ligand-to-metal charge transfer (LMCT) bands.\textsuperscript{226} Ni/Mg\textsubscript{1.3}AlO\textsubscript{1000} discloses a LMCT band with weaker intensity and blue shift compared to that of Ni/Mg\textsubscript{2}AlO\textsubscript{1000}. This reflects a higher Ni^{2+} dispersion, probably correlated with the stronger MSI of Ni/Mg\textsubscript{2}AlO\textsubscript{1000} \textsuperscript{27} Besides, modifying this material with La and CA-assisted synthesis shows further blue-shift of the UV band, indicating the formation of highly dispersed Ni^{2+} in LaNi(CA)/Mg\textsubscript{1.3}AlO\textsubscript{x}.

The UV-Vis-DR spectra in the region 350–800 nm (Figures 1c and 5.6) reveal the coordination of Ni\textsuperscript{2+}.\textsuperscript{[15,17,28]} The Ni catalysts expose mainly absorption bands at 400 nm and 660 nm, which are associated with \(\nu_1 (\text{A}_{2g} \rightarrow \text{T}_{2g})\) and \(\nu_2 (\text{A}_{2g} \rightarrow \text{T}_{1u})\) absorptions caused by Ni\textsuperscript{2+} species in octahedral coordination (Oh), similarly to that of Ni/MgO spectra, instead of tetrahedral (Th) geometries. Such lack of Ni\textsuperscript{2+} (Th) species reflects the presence of surplus MgO that stabilizes the Ni\textsuperscript{2+} species and suppresses the formation of NiAl\textsubscript{2}O\textsubscript{4} spinel.\textsuperscript{[29–31]}

The XRD pattern of LaNi(CA)/Mg\textsubscript{1.3}AlO\textsubscript{1000} proves the presence of the periclase (MgO) structure, suggesting formation of NiO–MgO solid solution (Figures 1a and S. 2). Hence, the shoulder at 400–600 nm in the UV-Vis-DR spectrum recorded for LaNi(CA)/Mg\textsubscript{1.3}AlO\textsubscript{1000} suggests local defect structures in NiO–MgO solid solution\textsuperscript{226} that can explain the \(\alpha\) reduction peak at 400 °C (Figure 1b).\textsuperscript{[21,24,32]} A similar shoulder is found in the UV-Vis spectra for Ni/MgO (Figure 1c) or LaNi/Mg\textsubscript{1.3}AlO\textsubscript{1000} (Figure S. 6) but with higher intensity/red shifts correlated to more Ni\textsuperscript{2+} species in the local defect structures.

The UV-Vis spectrum of Ni/Mg\textsubscript{1.3}AlO\textsubscript{1000} shows two bands at 400 nm and 660 nm (Figure 1c), which were also found for LaNi(CA)/Mg\textsubscript{1.3}AlO\textsubscript{x} and Ni/Mg\textsubscript{1.3}AlO\textsubscript{1000}. However, LaNi(CA)/Mg\textsubscript{1.3}AlO\textsubscript{1000} reveals only a strong broad band at 400 nm ending at 600 nm, quite similar to that of LaNi(CA)/MgO.

No Ni particles were observed in the representative STEM high-angle annular dark field (HAADF) image of fresh calcined LaNi(CA)/Mg\textsubscript{1.3}AlO\textsubscript{1000} (Figure S. 7). This result suggests, in accordance with the XRD patterns (Figure 1a) and UV-Vis-DRS data (Figure S. 5), that Ni\textsuperscript{2+} species are highly dispersed in the structure of the support.\textsuperscript{33} However, the EDX elemental maps and their corresponding HAADF image of this sample show the preferred location of Ni at Mg(La)-enriched regions with brighter contrast attributed to the high atom weight of La (Figure 2).

This was further validated by EDX spectra at regions 006 and 008, showing increased Ni concentration at Mg(La)-enriched locations (Figure S. 8). This preferred Ni location probably also proves the presence of NiO–MgO solid solution in LaNi(CA)/Mg\textsubscript{1.3}AlO\textsubscript{1000}. As a result, finely dispersed Ni\textsuperscript{2+} can only be partially reduced (Figure S. 4) and hardly aggregate to metallic Ni particles. However, good metal dispersion is achieved, and the particles are attached to the support (Figures S. 9b-2 and S. 10), mostly due to strong MSI of such NiO\textsubscript{x} and MgO in their solid solution.

The CH\textsubscript{4}-rich DRM tests show that the thermal pre-treatment of the Mg\textsubscript{2}AlO\textsubscript{x} support at 1000 °C remarkably improves the stability and coking resistance of the corresponding Ni catalysts in CH\textsubscript{4}-rich DRM (Figures 3 and 4a). The measured conversions were below calculated equilibrium data (Figures S. 11 and S. 12). LaNi(CA)/Mg\textsubscript{1.3}AlO\textsubscript{1000} showed improved resistance against deactivation (Figure 3) and carbon accumulation (Figure 4a), which can be assigned to its reducibility (Figure 1b) and finely dispersed Ni atoms maintained during the reaction (Figures S. 9b-2, S. 9c-2, S. 13). In contrast, Ni agglomeration occurred with Ni/Mg\textsubscript{2}AlO\textsubscript{x} already after the pre-reduction step and even more seriously during DRM (Figures S. 9b-1 and c-1) and led to bigger Ni particles that may cause serious deactivation and coking. The H\textsubscript{2}/CO ratios reach unity, especially at 750 °C, reflecting a low contribution of reverse water gas shift reaction which otherwise would deteriorate the H\textsubscript{2} yield at high temperature with CH\textsubscript{4}-rich feed (Figure S. 14).

At 750 °C, LaNi(CA)/Mg\textsubscript{1.3}AlO\textsubscript{1000}, as the best catalyst among samples with this support (Figure S. 14a–c), performs similarly to LaNi(CA)/Mg\textsubscript{2}AlO\textsubscript{x}. However, detected carbon amounts on spent samples of both catalysts after CH\textsubscript{4}-rich DRM differ significantly from each other.

The coke pathways were studied in a series of runs with catalyst Ni/Mg\textsubscript{1.3}AlO\textsubscript{x} at different temperatures (500–750 °C) using feeds composed of CH\textsubscript{4}/Ar = 1 or 2 (both without CO\textsubscript{2}) as well as CH\textsubscript{4}/CO\textsubscript{2} = 1 or 2 at a GHSV of 170 L/(g\textsubscript{cat}\_\text{dry}·h) (Figure 4b). The carbon deposits on spent samples were analyzed after 8 h on stream. At 500 °C, the carbon contents on all spent catalysts
were negligible, as methane decomposition (MD) and DRM (producing CO as a reactant for Boudouard reaction (BD)) run at higher temperatures. In all tests with Ni/Mg$_2$AlO$_x$ and CH$_4$/Ar, raising the temperature and CH$_4$ concentration caused a proportional rise in carbon deposition, reflecting the impact of methane decomposition and/or metal agglomeration.$^{[34–35]}$

When CO$_2$ was converted in DRM at 630°C with CH$_4$ at any portion, the deposition was significantly higher, indicating the extent of BD reaction via CO disproportionation, which out-numbered MD contribution. However, at 750°C, the contribution of BD decreased.$^{[36]}$ Indeed, when Ar is replaced by CO$_2$, the carbon deposition changes only slightly in case of CH$_4$/CO$_2$ = 2 but decreases dramatically at CH$_4$/CO$_2$ = 1 (higher CO$_2$ partial pressure), adapting to the thermodynamically favorable gasification (reversed BD) of C by CO$_2$, at high temperature.$^{[34,37]}$

These data suggest that La.Ni(CA)/Mg$_2$AlO$_x$ has a structure modification effect that can slow down BD reaction, lowering the coking rate at 630°C in CH$_4$-rich DRM (Figure 4a)$^{[32]}$. Nevertheless, at 750°C carbon mainly formed by MD reaction is still observed on all spent Mg$_2$AlO$_x$-supported Ni catalysts due to the lower concentration of CO$_2$ and low efficiency in activation of CO$_2$. However, such carbon deposition can also be suppressed by applying Mg$_2$AlO$_x$.1000 supported Ni catalysts (Figure S. 15).

Further coking tests with CH$_4$/Ar = 2 (no CO$_2$) at 750°C (Figure 4c) elucidate the specific influence of MD on carbon deposition. While Mg$_2$AlO$_x$ supported catalysts show similar or higher carbon contents after CH$_4$-rich DRM (CH$_4$/CO$_2$ = 2) than after MD (CH$_4$/Ar = 2), Ni/Mg$_2$AlO$_x$.1000 and especially La.Ni(CA)/Mg$_2$AlO$_x$.1000 form lower amounts of carbon in CH$_4$-rich DRM compared to MD. This contrast points to the high potential of the latter catalysts in CO$_2$ activation, even at low partial pressure, which cannot be achieved with Ni catalysts supported on Mg$_2$AlO$_x$. The CO$_2$ activation, in this case, reduced the coke deposition by MD reaction in CH$_4$-rich DRM by enhancing carbon gasification.

The clearly enhanced CO$_2$ activation by La.Ni(CA)/Mg$_2$AlO$_x$.1000 in CH$_4$-rich DRM might be attributed to the stronger influence of MgO on Ni finely dispersed in NiO–MgO solid solution than in Ni/Mg$_2$AlO$_x$ or La.Ni(CA)/
In the first step of the reaction, this structure is supposed to accelerate the \( \text{CO}_2 \) dissociation at the metal-support interface as well as the \( \text{CH}_4 \) cracking on Ni atoms,\(^{41-46}\) thereby releasing the first CO and \( \text{H}_2 \) molecules.\(^{115}\) With \( \text{La}_2 \text{O}_3/ \text{La}_2 \text{O}_3 \text{CO}_3 \) enriched around these metal atoms (Figure 2), defective sites (e.g. oxygen vacancies) are generated (Figure 1c), promoting dissociative \( \text{CO}_2 \) adsorption which subsequently forms surface oxygen species.\(^{114,115-118}\) The increased availability of these oxygen species transforms carbonaceous intermediates from \( \text{CH}_4 \)-rich mixture and releases second CO and \( \text{H}_2 \) (Table S. 1). This behavior enhances both the reaction rate and the carbon resistance of the catalyst even at low \( \text{CO}_2 \) partial pressure. Such solid solution was recently also supposed to be beneficial for \( \text{CH}_4 \)-rich DRM by suppressing carbon formation.\(^{41,42}\) However, concerning the loading of Ni and the catalyst productivity in that investigation (Table S. 3), the catalyst in the present study is superior. It should be noted that the mentioned NiO–MgO interaction is expected in Ni/MgO as well. However, due to low Ni loading, this sample showed almost no activity due to low Ni surface concentration.

\( \text{LaNi(CA)/Mg}_2 \text{AlO}_4 \cdot 1000 \) was employed in a long-term test over 100 h at typical conditions to evaluate the application potential (Figure 5). In known literature,\(^{19}\) a long-term \( \text{CH}_4 \)-rich DRM run with such high feed rate was not reported.

**Experimental Section**

\( \text{Mg–Al} \) mixed oxide supports were prepared from \( \text{Mg}–\text{Al} \) hydrotalcite (Pural MG50, Sasol). The default precursor \( \text{Mg}_2 \text{AlO}_4 \) was obtained by calcining the \( \text{Mg}–\text{Al} \) hydrotalcite at 550 °C. This material was thermally pre-treated at 1000 °C with a rate of 2 K/min to prepare \( \text{Mg}_2 \text{AlO}_4 \cdot 1000 \) support.

In order to prepare the final catalysts, both supports were treated with \( \text{Ni(NO}_3\text{)}_2 \cdot 6\text{H}_2\text{O} \) (99 %, Alfa Aesar) and \( \text{La(NO}_3\text{)}_3 \cdot 6\text{H}_2\text{O} \) (99 %, ABCR GmbH) by wet impregnation (nominal Ni content 2.5 wt%). Citric acid (> 99 %, Alfa Aesar) was added simultaneously in some cases. The molar ratio of La and Ni was set to 0.8, and the Ca/metal molar ratio was fixed at 1.5. The calculated amounts of Ni, La precursors and CA were dissolved in deionized water and the solution was stirred for 4 h at 50 °C. The \( \text{Mg–Al} \) supports were then added and the slurry was stirred at 60 °C for 15 h. Water was gradually removed by a rotary evaporator for 4 h and the samples were dried overnight at 120 °C and calcined at 400 °C for 3 h and then at 800 °C for 6 h both in air with a rate of 2 K/min. MgO (FLUKA) as well as its corresponding Ni-loaded samples \( \text{LaNi(CA)/MgO} \) and Ni/MgO served as reference materials. Pure NiO was prepared by calcining \( \text{Ni(NO}_3\text{)}_2 \cdot 6\text{H}_2\text{O} \) at 800 °C.

XRD powder patterns were recorded on a Panalytical X’Pert diffractometer equipped with a Xcelerator detector using automatic divergence slits and Cu Kα1/α2 radiation (40 kV, 40 mA; λ = 0.15406 nm, 0.154443 nm). Cu beta-radiation was excluded using a nickel filter foil. The samples were mounted on silicon zero background holders. The obtained intensities were converted from automatic to fixed divergence slits (0.2°) for further analysis. Peak positions and profile were fitted with Pseudo-Voigt function using the HighScore Plus software package (Panaanalytical). Phase identification was done by using the PDF-2 database of the International Center of Diffraction Data (ICDD).

The low-temperature \( \text{N}_2 \) adsorption was performed on a Micromeritics ASAP 2010 apparatus at −196 °C. The samples were degassed at 200 °C in vacuum for 4 h before the analysis.

**Figure 5.** \( \text{CH}_4 \), \( \text{CO}_2 \) conversions and \( \text{H}_2/\text{CO} \) ratio in long-term \( \text{CH}_4 \)-rich DRM with \( \text{LaNi(CA)/Mg}_2 \text{AlO}_4 \cdot 1000 \) (750 °C, 1 bar, \( \text{CH}_4/\text{CO}_2 = 2 \), GHSV = 170 L/\((\text{gcat} \times \text{h}) \)). Catalyst was pre-reduced in situ at 700 °C for 1.5 h.
The metal (Ni, Mg, Al, La) contents of the samples were determined by ICP-OES using a 715-ES device (Varian).

The carbon deposition on spent catalysts was analyzed using a TruSpec Micro CHNS analyzer (LECO Corporation). Up to 10 mg of the investigated sample were catalytically burned with oxygen in a helium stream at 1100 °C. The resulting gas was analyzed with an infrared detector and a thermal conductivity detector.

H₂-TPR experiments were performed with a Micromeretics Autochem II 2920 instrument with a thermal conductivity detector. A 300 mg sample was loaded into a U-shaped quartz reactor and heated in 5%O₂/H₂ (50 ml/min; r.t. to 400 °C with 20 K/min, 30 min hold, then cooled to r.t. in Ar flow). TPR run was made up to 1000 °C in 5%H₂/Ar (50 ml/min; 10 K/min, final hold 30 min before cooling to r.t.). A TPR for pre-reduced sample was also conducted. After oxidation with 5%O₂/He, the sample was pre-reduced in pure H₂ (50 ml/min) at 700 °C for 1.5 h to imitate the pretreatment in DRM setup. Then the system was cooled to r.t. and a regular TPR experiment was appended. The H₂ consumption peaks were recorded using a thermal conductivity detector.

XPS measurements were carried out with an ESCALAB 220iXL instrument (Thermo Fisher Scientific) with monochromatic Al Kα radiation (E = 1486.6 eV). Samples were prepared on a stainless-steel holder with conductive double sided adhesive carbon tape. The electron binding energies were obtained with charge compensation using a flood electron source and referenced to the C1s peak of adventitious carbon at 284.8 eV (C–C and C–H bonds). The peaks were deconvoluted with Gaussian-Lorentzian curves using the software Unifit.

UV-Vis-DR spectra were measured over 200–800 nm using a Cary 5000 spectrometer (Varian) equipped with a diffuse reflectance accessory (praying mantis, Harrick). BaSO₄ was used as a white reference standard and diluted material was used for the measurement with pure NiO because of its high Ni content.

STEM measurements were performed at 200 kV with an aberration-corrected JEM-ARM200F (JEOL, Corrector: CEOS). The microscope is equipped with a JED-2300 (JEOL) energy-dispersive X-ray-spectrometry (EDXS) for chemical analysis. The aberration-corrected STEM imaging (High-Angle Annular Dark Field (HAADF) and Annular Bright Field (ABF)) was performed under the following conditions: HAADF and ABF both were done with a spot size of approximately 0.13 nm, a convergence angle of 30–36° and collecting at semi-angles for HAADF and ABF of 90–170 mrad and 11–22 mrad, respectively. The sample was dry deposited without any pretreatment on a holey carbon film supported by a Cu-grid (300 mesh) and transferred to the microscope.

DRM tests were carried out with a fixed-bed continuous-flow quartz reactor (1 bar, GHSV = 170 L/(gcat×h); 500–750 °C; 50 mg catalyst, grain size < 315 μm, diluted by 2 g of quartz). After in situ pre-reduction with pure H₂ (700 °C, 100% H₂, 50 ml/min, 1.5 h), the temperature was adjusted and held for 8–100 h on stream. The feed was composed of 80 vol% CH₄ in He (pre-mixed, Air Liquide) and admixed pure CO₂ (Linde) to set CH₄/CO₂ = 1 or 2. Volumetric flow rates given in this study are related to 25 °C and 1 bar. He served as an internal standard for volume change determination during the reaction. Feed and product gases were analyzed by an on-line gas chromatograph (Agilent 6890) equipped with flame ionization detector (HP Plot Q capillary, 15 m × 0.53 mm × 40 μm) and thermal conductivity detector (Carboxene packed, 4.572 mm × 3.175 mm) for analysis of hydrocarbons and permanent gases, respectively. Pure components were used as references for peak identification and calibration. Carbon balances were calculated from gas products reaching more than 97%. Conversions and H₂/CO ratio were calculated from mole streams of fed and converted reactants.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: dry reforming of methane · model biogas and natural gas · Ni catalyst · non-stoichiometric DRM · stability

[1] I. Yildiz, in Comprehensive Energy Systems (Ed.: I. Dincer), Elsevier, Oxford, 2018, pp. 521–567.
[2] S. Faramawy, T. Zaki, A. A. E. Sakr, J. Nat. Gas Sci. Eng. 2016, 34, 34–54.
[3] BP Statistical Review of World Energy: 2019, https://www.bp.com/content/dam/bp/business-sites/en/global/corporate/pdf/energy-economics/statistical-review/bp-stats-review-2019-full-report.pdf
[4] N. Abatzoglou, S. Boivin, Biofuels Bioprod. Biorefin. 2009, 3, 42–71.
[5] C. Papadopoulou, H. Matralis, X. Verykios, in Catalysis for Alternative Energy Generation (Eds.: L. Gucci, A. Erdelyi), Springer, New York, 2012, pp. 57–127.
[6] F. Gerner; Vietnam: Maximizing finance for development (MFD) energy infrastructure assessment program, 2018; https://ausschamsvn.org/wp-content/uploads/2018/05/1.-WB_March-2018-Vietnam-Energy-Sector-Assessment.pdf
[7] D. d. Graaf, R. Fendler; Biogas production in Germany; 2010; http://www.spin-project.eu/downloads/0_Background_paper_biogas_Germany_en.pdf.
[8] G. J. Bradford, M. A. Vannice, Catal. Rev. Sci. Eng. 1999, 41, 1–42.
[9] A. N. Şener, M. E. Gunay, A. Leba, R. Yildirim, Catal. Today, 2018, 289, 302–309.
[10] M. Usman, W. M. A. Wan Daud, H. F. Abbas, Renewable Sustainable Energy Rev. 2015, 45, 710–744.
[11] N. A. K. Aramouni, J. G. Touma, B. A. Tarboub, J. Zeaiter, M. N. Ahmad, Renewable Sustainable Energy Rev. 2018, 82, 2570–2585.
[12] Q. L. M. Ha, U. Armbruster, C. Kreyenschulte, H. Atia, H. Lund, H. T. Vuong, S. Wohlrab, Catal. Today, 2019, 334, 203–214.
[13] P. Kirm, C. J. Lee, Catalysts 2018, 8, 361.
[14] P. A. Kumar, M. P. Reddy, B. Hyun-Sook, H. H. Phil, Catal. Lett. 2009, 131, 85–97.
[15] S. Damyanova, B. Pawelec, K. Aritshtrova, J. L. G. Fierro, Int. J. Hydrogen Energy 2012, 37, 15966–15975.
[16] M. Serra, P. Salagre, Y. Cesteros, F. Medina, J. E. Sueiras, Phys. Chem. Chem. Phys. 2004, 6, 858–864.
[17] C. Jiménez-González, Z. Boukhla, B. de Rivas, J. R. González-Velasco, J. I. Gutiérrez-Ortiz, R. López-Fonseca, Energy Fuels 2014, 28, 7109–7121.
[18] A. Cimino, D. Gazzoli, V. Indovina, G. Moretti, M. Occhiuzzi, F. Pepe, Top. Catal. 1999, 8, 171–178.
[19] E. Buckenstein, Y. Hang Hu, Appl. Catal. A 1999, 183, 85–92.
[20] F. Arena, L. Licciardello, A. Parmaliana, Catal. Lett. 1990, 6, 139–149.
[21] M. Jafarbegloo, A. Tarlani, A. W. Mesbah, J. Muzart, S. Sahebdelfar, Catal. Lett. 2016, 146, 238–248.
[22] C. Li, Y.-W. Chen, Thermochim. Acta 1995, 256, 457–465.
[23] Q. Zhang, K. Long, J. Wang, T. Zhang, Z. Song, Q. Lin, Int. J. Hydrogen Energy 2017, 42, 14103–14114.
[24] S. L. González-Cortés, I. Aray, S. M. A. Rodulfo-Baechler, C. A. Lugo, H. L. Del Castillo, A. Loaiza-Gil, F. E. Imbert, H. Figueroa, W. Pernia, A.
Rodríguez, O. Delgado, R. Casanova, J. Mendialdua, F. Rueda, J. Mater. Sci. 2007, 42, 6532–6540.

[25] Q. L. M. Ha, U. Armbruster, H. Atia, M. Schneider, H. Lund, G. Agostini, J. Radnik, H. T. Vuong, A. Martin, Catalysis 2017, 7, 157.

[26] B. Scheffler, J. J. Heijenring, J. A. Moulijn, J. Phys. Chem. 1987, 91, 4752–4759.

[27] J. Escobar, J. Antonio De Los Reyes, T. Viveros, Appl. Catal. A 2003, 253, 151–163.

[28] A. Zecchina, G. Spoto, S. Coluccia, E. Guglielminotti, J. Chem. Soc. Faraday Trans. 1 1984, 80, 1875–1889.

[29] L. Zhang, Q. Zhang, Y. Liu, Y. Zhang, Appl. Surf. Sci. 2016, 389, 25–33.

[30] R. Zhang, G. Xia, M. Li, Y. Wu, H. Nie, D. Li, J. Fuel Chem. Technol. 2015, 43, 1359–1365.

[31] Z. Boukha, C. Jiménez-González, M. Gil-Calvo, B. de Rivas, J. R. González-Velasco, J. I. Gutiérrez-Ortiz, R. López-Fonseca, Appl. Catal. B 2016, 199, 372–383.

[32] A. Zecchina, G. Spoto, S. Coluccia, E. Guglielminotti, J. Chem. Soc. Faraday Trans. 1 1984, 80, 1891–1901.

[33] D. Li, R. Li, M. Lu, X. Lin, Y. Zhan, L. Jiang, Appl. Catal. B 2017, 200, 566–577.

[34] S. Wang, G. Q. Lu, G. J. Millar, Energy Fuels 1996, 10, 896–904.

[35] M. Argyle, C. Bartholomew, Catalysis 2015, 5, 145.

[36] M.-S. Fan, A. Z. Abdullah, S. Bhatia, ChemCatChem 2009, 1, 192–208.

[37] D. Pakhare, J. Spivey, Chem. Soc. Rev. 2014, 43, 7813–7837.

[38] E. Ruckenstein, Y. H. Hu, Appl. Catal. A 1995, 133, 149–161.

[39] S. Helveg, C. López-Cartes, J. Sehested, P. L. Hansen, B. S. Clausen, J. R. Rostrup-Nielsen, F. Abdil-Pedersen, J. K. Narskov, Nature 2004, 427, 426–429.

[40] H. S. Bengaard, J. K. Narskov, J. Sehested, B. S. Clausen, L. P. Nielsen, A. M. Molenbroek, J. R. Rostrup-Nielsen, J. Catal. 2002, 209, 365–384.

[41] K. Tomishige, O. Yamazaki, Y. Chen, K. Yokoyama, X. Li, K. Fujimoto, Catal. Today 1998, 45, 35–39.

[42] M. García-Diéguez, C. Herrera, M. A. Larrubia, L. J. Alemany, Catal. Today 2012, 197, 50–57.

[43] Z. Zhang, X. E. Verykios, S. M. MacDonald, S. Affrossman, J. Phys. Chem. 1996, 100, 744–754.

[44] X. E. Verykios, Int. J. Hydrogen Energy 2003, 28, 1045–1063.

[45] E. Ruckenstein, Y. H. Hu, Catal. Lett. 1998, 57, 183–185.

[46] P. M. Mortensen, I. Dybkjaer, Appl. Catal. A 2015, 495, 141–151.

[47] M. Yu, K. Zhu, Z. Liu, H. Xiao, W. Deng, X. Zhou, Appl. Catal. B 2014, 148–149, 177–190.

[48] A. T. Ashcroft, A. K. Cheetham, M. L. H. Green, P. D. F. Vernon, Nature 1991, 352, 225.

[49] A. Horváth, G. Stefler, O. Geszti, A. Kienneman, A. Pietraszek, L. Guczi, Catal. Today 2011, 169, 102–111.

[50] J. Károlyi, M. Németh, C. Evangelisti, G. Sáfárán, Z. Schay, A. Horváth, F. Somodi, J. Ind. Eng. Chem. 2018, 58, 189–201.

[51] M. Németh, D. Sránkó, J. Károlyi, F. Somodi, Z. Schay, G. Sáfárán, I. Sajó, A. Horváth, Catal. Sci. Technol. 2017, 7, 5386–5401.

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