Enhanced activity in methane dry reforming by CO₂ induced metal-oxide interface restructuring of Ni/ZrO₂

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Abstract: The activity of Ni/ZrO₂ catalysts for dry reforming of methane is significantly enhanced by activation and regeneration in presence of CO₂. The exposure to CO₂ maximizes and dynamically restructures the Ni-ZrO₂ interface, which is critical for obtaining stable catalysts. The ZrO_{2-x} at this interface acts catalytically by accepting and transferring one oxygen of CO₂ to the Ni surface, releasing CO in the decomposition of transiently formed carbonates. This opens a fast additional reaction pathway to convert CO₂, eclipsing the direct CO₂ dissociation on Ni. The kinetically controlled availability of atomic oxygen via this pathway reduces the carbon concentration on the surface, leading to less refractory carbon deposition and a more facile regeneration.

Dry reforming of methane (DRM), CO₂ + CH₄ ⇌ 2 CO + 2 H₂, leads to synthesis gas with H₂/CO ratios close to one and is frequently used to decrease this ratio in combined CH₄ reforming processes. To reach acceptable conversion levels, temperatures around 900 K are required.^[1] While the activity is usually adjusted via the reaction temperature, stabilizing the catalyst against sintering and kinetically minimizing concentration of carbon deposits are critical challenges for the application on an industrial scale.^[2] The large number of units installed to produce synthesis gas (worldwide 2378 units in operation in 2014 with a power equivalent of 117 GW thermal output)^[3] require highly active, but also stable catalysts.^[4] Noble and base metals can be used as catalytically active components, however, the large volume of the catalysts required for methane reforming allows only base metal catalysts such as Ni and Co to be economically feasible.^[5]

For stabilizing the catalyst activity, the support plays an important role and its functionality at the metal support interface with respect to catalytic activity has been vividly debated.^[6] Hypothesizing that CO₂ reduction may require a reducible oxide support Montoya et al. used a Ce doped ZrO₂ support to show oxygen mobility at the metal-support interface to be crucial for a stable catalyst.^[7] Odedairo et al. reported that a plasma treatment of Ni/CeO₂ enhances the metal support interface and generates a clean metal surface, both effects leading to a higher activity in methane dry reforming.^[6b] Rezaei et al. have increased the metal support interface via synthesis of a high surface area CeO₂-ZrO₂.^[6d, 6e] In contrast, Iglesia et al. concluded that the activity is only related to the type of the active metal and its particle size, leaving the

reaction conditions to be most significant for catalyst stability.^[8] They proposed that the C-H bond breaking of CH₄ on the active metal is the rate determining step. Bitter et al. described a bifunctional mechanism for dry reforming of methane over Pt/ZrO₂ catalysts, where CH₄ is decomposed forming H* and CH_x* species on the metal surface, while CO₂ is predominantly adsorbed at the support forming carbonates.^[9]

Although great effort has been made in the development of a stable catalyst for methane dry reforming, carbon deposits might be formed as the reacting gas composition in dry reforming favors carbon formation thermodynamically. These carbon deposits have to be removed periodically by oxidative treatments, which pose a challenge for catalyst stability in itself, as the oxidation of carbon deposits with O₂ is a highly exothermic reaction and the additional heat generated can induce catalyst deactivation due to sintering. Therefore, a thermally less demanding method to periodically remove carbon deposits has to be developed.

We report here a general concept for stable operation of Ni based catalysts for DRM, employing three approaches in parallel. We combine (i) a lower rate of coke formation by generating labile oxygen from CO₂ through CO₂ induced nano-restructuring of the Ni-ZrO₂ interface (ii) the stabilization of small metal domains at this interface via strong metal-support interactions, and (iii) the removal of deposited carbon via the thermally less taxing reverse Boudouard reaction (compared to the conventional regeneration with O₂). The key to enable this concept is a reducible support that interacts moderately strong with CO₂, allowing transiently formed carbonates to dynamically adjust the Ni metal oxide interface and to generate sites which provide oxygen for the reforming process itself as well as for the regeneration of the coked catalyst. We will show that exposing a Ni/ZrO₂ catalyst to CO₂ allows to maximize this interface and leads to a highly active catalyst. This will be combined with a periodic oxidative treatment in CO₂ for coke removal, which has no adverse effect on the activity of the catalyst compared to the regeneration in O₂. It has to be mentioned that this procedure has also an advantage from the point of operating the reaction on industrial scale. When using CO₂, regeneration can be initiated by removing CH₄ from the reactant gas (leaving the flow of CO₂) and after regeneration is completed the reaction can be started again by adding CH₄ to the reactant gas stream. This allows to avoid an additional purging of the reactor with inert gas, which is otherwise necessary if diluted O₂ is used for oxidative coke removal. Combining steady state and transient kinetic measurements with X-ray absorption spectroscopy (XAS) the role of the individual steps for this new concept will be deduced.

The reaction rates for CH₄ conversion in DRM of Ni supported on SiO₂, Al₂O₃ and ZrO₂ at 1073 K are shown as a function of time on stream in Figure 1 (for additional kinetic data see Figure S1 and S2). In the first 90 minutes the rates on the three catalysts were similar and decreasing with time on stream. At this point, the

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reaction was stopped and the catalysts were exposed to a stream of 100 % CO₂ at 1073 K for 90 minutes. After this step the rate on Ni/ZrO₂ increased markedly, approaching the initial reaction rate of CH₄ decomposition at 1073 K (red line in Figure 1) calculated from the rates for dry reforming and CH₄ conversion reported in literature.^[8] For Ni/Al₂O₃ and Ni/SiO₂, the exposure to CO₂ did not affect the course of deactivation. As all catalyst were carbon-free after regeneration in CO₂ (see Figure S3), we conclude that for Ni/ZrO₂ continued exposure to 1073 K did not induce sintering or surface reactions of Ni. Two subsequent cycles with CO₂ exposure followed by DRM demonstrate that periodical reactivation of Ni/ZrO₂ with CO₂ restitutes the activity of Ni/ZrO₂. It is interesting to note that treatment with CO₂ at 1073 K before DRM (after reduction in 10% H₂ at 873 K) increased the reaction rate to the level it reached otherwise after regeneration, which is about a factor of 2 higher, while exposure to He at 1073 K did not affect the activity.

Figure 1. DRM rates for (■) Ni/ZrO₂, (●) Ni/Al₂O₃, (▲) Ni/SiO₂ and (▼) CO₂ treated Ni/ZrO₂ at 1073 K before reaction. The catalysts were treated in 100 % CO₂ in the sections indicated. The dashed red line designates the initial reaction rate for CH₄ decomposition at 1073 K calculated from the data in reference [8].

In situ XAS at the Ni K-edge was used to monitor the oxidation state of Ni during the cycles of DRM and CO₂ treatment (Figure 2). During the first dry reforming cycle (after reduction in H₂ flow 10 % H₂ in He, 1 bar, 873 K, 90 min) the shape of the white line (indicated by an arrow in Figure 2 A) and the pre-edge shoulder at 8330 eV in the XANES of Ni (Figure 2 A) showed that Ni/SiO₂ and Ni/ZrO₂ were fully reduced. The slightly higher white line for Ni/Al₂O₃ is attributed to a small fraction of oxidized Ni, present as Ni²⁺ in Ni aluminate.^[10] After exposing the catalyst to CO₂ at 1073 K, the intensity of the white line increased sharply for all catalysts, indicating that Ni was oxidized. The comparison of the height and shape of the peak above the absorption edge with bulk NiO (black curve in Figure 2 B) indicates that Ni²⁺ was oxidized to Ni²⁺ in all catalysts. After reverting back to the DRM gas composition, Ni/SiO₂ and Ni/ZrO₂ were fully reduced, while Ni/Al₂O₃ remained partially oxidized, which is attributed to the presence of NiAl₂O₄ (Figure 2 C).

It would be conceivable that the increase in the DRM rate after exposure to CO₂ is associated with the formation of smaller Ni particles formed during exposure to CO₂, as observed by Gonzalez during the exposure of a Ni/ZrO₂ catalyst to CO.^[11] Therefore, the EXAFS before and after CO₂ treatment was

measured to determine potential changes in the particle size (Figure S4 and Table S1-S4). All catalysts showed a similar particle size of around 3 nm after the first reaction cycle. NiO was observed for Ni/ZrO₂ and Ni/SiO₂ after CO₂ exposure and both catalysts were reduced after changing back to the reactant gas, as concluded by the disappearance of the Ni-O contributions and the presence of short Ni-Ni distances. Also Ni/Al₂O₃ showed Ni-Ni contributions from reduced Ni after the exposure to reactant gases, however, larger Ni-Ni distances and Ni-O contributions were still present resulting from the progressive formation of NiAl₂O₄. We attribute the continued decrease in activity for Ni/Al₂O₃ to this process.^[12]

Figure 2. XANES recorded at the Ni K-edge of 5 wt.% Ni/ZrO₂ (blue), 5 wt.% Ni/SiO₂ (orange) and 5 wt.% Ni/Al₂O₃ (green) during the first DRM reaction cycle at 1073 K (A), during the subsequent exposure to CO₂ at 1073 K (B) and during the second DRM cycle at 1073 K (C). XANES of Ni foil and bulk NiO are included for comparison (black).

The coordination number of Ni/SiO₂ increased after CO₂ treatment, indicating that the particles had strongly sintered (particle size 10 nm). In contrast, the Ni-Ni coordination number for Ni/ZrO₂ was unaffected. The difference in the average coordination numbers of Ni over the three catalysts after exposure to CO₂ demonstrates that only ZrO₂ was able to efficiently stabilize the Ni particles. A control experiment using O₂ instead of CO₂ for regeneration (Figure S5) showed that the DRM activity also decreased for Ni/ZrO₂. This is attributed to sintering of metal particles, caused by the strongly exothermic oxidation with O₂. In contrast, the removal of carbon deposits via the reversible Boudouard reaction as well as the oxidation of the metal particles with CO₂ is endothermic (Table 1). Note that this endothermic cleaning of the metal surface did not stabilize Ni supported on Al₂O₃ and SiO₂, i.e., the rate of methane conversion was lower on Ni/Al₂O₃ and Ni/SiO₂ after removal of carbon.

Table 1. Reaction equations and corresponding reaction enthalpies for different oxidation reactions of Ni and carbon.

1.	CO ₂ + C ⇌ 2CO	ΔH ⁰ = 169.9 kJ mol ⁻¹
2.	Ni + CO ₂ ⇌ NiO + CO	ΔH ⁰ = 47.1 kJ mol ⁻¹
3.	C + O ₂ ⇌ CO ₂	ΔH ⁰ = -394.8 kJ mol ⁻¹
4.	2Ni + O ₂ ⇌ 2NiO	ΔH ⁰ = -235.2 kJ mol ⁻¹

In order to characterize the chemical interactions of CO₂ with ZrO₂, XANES of highly dispersed ZrO₂ on SiO₂ were measured. This high dilution was required to monitor changes in the local

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environment of the Zr atoms during CO₂ exposure, as for conventional Ni/ZrO₂ catalyst the large number of Zr atoms in the solid bulk phase would not allow to identify subtle changes in its chemical state. XANES were recorded at the Zr-K edge in He at 1073 K (after reduction at 873 K), during the first reaction cycle, the first CO₂ cycle and the second reaction cycle (Figure 3). After the initial reduction at 873 K the highest intensity of the pre-edge peak at 18000 eV (Figure 3 B) was observed. This absorbance is assigned to the 1s-4d transition,^[13] which is forbidden in a centrosymmetric environment.^[14] Thus, the appearance of this peak indicates a distortion of the Zr-O geometry, which results from the removal of one oxygen and leads to the formation of an oxygen vacancy at the metal support interface. In reaction atmosphere, the intensity of this pre-edge peak decreased, caused by saturation of the oxygen vacancies with oxygen from CO₂ and the resulting restoration of the centrosymmetry. This indicates that under steady state reaction conditions the presence of CO₂ increased the pool of labile oxygen species i.e., oxygen that is readily removed in reductive atmosphere, thus, enhancing the available oxygen that can be spilled over to Ni.^[8-9] In order to exclude that the XANES at the Zr-K edge is affected by structural changes in the SiO₂-ZrO₂ mixed oxide, the reduction/reaction cycle was carried out in absence of Ni, where changes in the XANES were not observed (Figure S6)

Figure 3. XANES at the Zr K-edge recorded at 1073 K of a 5 wt.% Ni/ZrO₂-SiO₂ after reduction at 873 K in 10% H₂ in He (black), during the first DRM reaction cycle at 1073 K (blue), the subsequent exposure to CO₂ (purple) and the second DRM reaction cycle (yellow). (A) XANES at the Zr K-edge and (B) magnification of the region assigned to the 1s – 4d transition.

To further analyze the impact of the support on the kinetics of the individual reaction steps, QEXAFS with a time resolution of 2 Hz were recorded during switching from He to CO₂ over Ni/SiO₂, untreated and CO₂ treated Ni/ZrO₂ (Figure 4 A). The oxidation rate of Ni by CO₂ depended strongly on the support (Figure 4 B). Exposure of Ni/ZrO₂ to CO₂ led to a rapid oxidation of Ni, while Ni/SiO₂ was oxidized at a lower rate. It should be emphasized that CO was the only product formed after exposing both catalysts to CO₂ (Figure S7). As the average particle size of Ni on both supports was similar (EXAFS analysis), the higher oxidation rate of Ni/ZrO₂ by CO₂ suggests a higher rate of reactive oxygen formation. Thus, we conclude that the oxygen vacancies of ZrO₂ aided the dissociation of CO₂ compared to the metal surface. As rate of oxygen formation from CO₂ dissociation on Ni would hardly differ between Ni/SiO₂ and Ni/ZrO₂, differences in the oxidation rate should not occur. In Ni/ZrO₂ CO₂ can be activated at the metal support interface^[15], thus we attribute the higher oxidation rate of Ni/ZrO₂ ($k = 0.19 \text{ s}^{-1}$) compared to Ni/SiO₂ ($k = 0.04 \text{ s}^{-1}$) to the additional availability of oxygen atoms provided by ZrO₂

interface sites. Repeated exposure of Ni/ZrO₂ to CO₂ with intermittent reduction led to a further enhancement of the rate of oxidation of Ni ($k = 0.48 \text{ s}^{-1}$, grey dataset in Figure 4), which we assign to an increase in the interface between Ni and ZrO₂.

Figure 4. Variation of Ni²⁺ concentration (A) deduced by linear combination fitting of QEXAFS data after switching from He to CO₂ and analysis of the (1st order) rate constant for the oxidation reaction (B): Ni/SiO₂ (orange), Ni/ZrO₂ after reduction (blue) and Ni/ZrO₂ after CO₂ treatment (grey).

The identical apparent activation energies (87 ± 2 kJ/mol, Figure S8) for DRM across the whole temperature range explored indicate an identical reaction mechanism for CO₂ treated and untreated Ni/ZrO₂.^[2] It has been paradigmatically stated in literature e.g.^[8, 16] that C-H activation is rate determining for DRM. Thus the increase of the pre-exponential factor by 2.5 times, has to result from a higher concentration of metal sites available for CH₄ conversion after exposure to CO₂. It has to be noted that the increase in CH₄ turnover rate by regeneration and the increase of the rate of oxidation of Ni were accidentally equal (i.e., both increased approximately 2.5 times).

In order to independently determine the concentration of the metal sites on the particles and sites at the metal support interface, IR spectra of adsorbed CO were used (Figure 5 and Table S5). The bands of adsorbed CO above 2000 cm⁻¹ are typical for linearly bonded CO on Ni.^[17] The shoulder observed above 2100 cm⁻¹ is attributed to CO adsorbed on partially oxidized Ni.^[17-18] As the intensity of CO adsorbed on partially oxidized Ni is only 10% of the intensity of the all bands assigned to CO (assuming identical absorption coefficients) the concentration of this species is too low to be identified in the XANES. Goodman et al. observed a band at 2086 cm⁻¹ for Ni/SiO₂ and assigned it to a weaker metal-CO interaction,^[19] which resulted from charge transfer from the small metal particles to the oxide support. Following this assignment we attribute the band at 2085 cm⁻¹ to CO adsorbed on Ni at the metal support interface.^[19] and the bands below 2070 cm⁻¹ to CO adsorbed on isolated Ni atoms.

Figure 5. IR spectra of CO adsorbed at 5 mbar followed by evacuation on the untreated (A) and CO₂ treated (B) Ni/ZrO₂ catalyst.

Note that this allows to differentiate the undisturbed sites on the metal surface (bands below 2075 cm^{-1}) and sites in vicinity of the ZrO_2 support (band at 2085 cm^{-1}). After CO_2 exposure, the intensity of the sum of the bands attributed to Ni surface sites increased by a factor of 2.9 (pointing to a three-fold higher concentration of accessible Ni, when assuming an identical adsorption coefficient of CO on Ni), while the band at 2085 cm^{-1} increased nearly by a factor of 2. Most importantly the use of CO as probe molecule shows that the Ni sites adjacent to a defect vary in concentration exactly in proportion to the increase in rate of CO_2 reduction during DRM.

This shows that exposure of Ni/ZrO_2 to CO_2 at high temperatures enhances the activity of the catalysts for DRM as well as the rate of oxidation of reduced Ni particles. The exposure to CO_2 increases the concentration of sites at the interface between the support and the metal, leading to coordinatively unsaturated zirconia at the interface, which is able to transiently form carbonates and dissociate these into CO and labile oxygen that can migrate across the metal particle. The proposed reaction mechanism is illustrated in Figure 6. The increase in rate is attributed to a higher concentration of accessible Ni metal sites. The stability is enhanced by the presence of labile atomic oxygen, which readily oxidizes surface carbon formed during the dissociation of methane. The generation of this labile oxygen through transiently formed carbonates at the metal support interface increases in parallel the fraction of accessible Ni surface sites. In DRM, this effect causes the approximately three-fold higher rate of CO formation by providing additional oxygen to remove carbon formed by the rate determining CH_4 dissociation.

During regeneration, the availability of oxygen via this route leads to the formation of CO via the (endothermic) Boudouard reaction, which is not as thermally demanding than the more conventional (exothermic) regeneration with O_2 with respect to heat evolution. While the nature of the ZrO_2 species at the Ni particles cannot be deduced from the current experiments, all observations are consistent with the fact that treatment with CO_2 maximizes the accessible ZrO_2 - Ni boundary as well as the concentration of metal surface sites. Overall, the results show that (inexpensive) Ni can be successfully used as catalyst in methane dry reforming, when ZrO_2 is used as support, generating a highly dynamic catalyst, which restructures itself during catalysis and regeneration by CO_2 on a nanoscopic level.

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Keywords: catalyst regeneration, heterogeneous catalysis, methane dry reforming, nickel catalysts, X-ray absorption spectroscopy

Figure 6. Schematic representation of the elementary steps of CO_2 treatment.

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