Enhanced activity in methane dry reforming by CO$_2$ induced metal-oxide interface restructuring of Ni/ZrO$_2$

Matthias Steib\dagger, Yu Lou\dagger, Andreas Jentys and Johannes A. Lercher*\* 

Abstract: The activity of Ni/ZrO$_2$ catalysts for dry reforming of methane is significantly enhanced by activation and regeneration in presence of CO$_2$. The exposure to CO$_2$ maximizes and dynamically restructuring the Ni-ZrO$_2$ interface, which is critical for obtaining stable catalysts. The ZrO$_2$-Ce$_x$ at this interface acts catalytically by accepting and transferring one oxygen of CO$_2$ to the Ni surface, releasing CO in the decomposition of transiently formed carbonates. This opens a fast additional reaction pathway to convert CO$_2$, eclipsing the direct CO$_2$ 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), CO$_2$ + CH$_4$ \approx \text{2 CO + 2 H}_2$, leads to synthesis gas with H$_2$/CO ratios close to one and is frequently used to decrease this ratio in combined CH$_4$ 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.\[5\] Hypothesizing that CO$_2$ reduction may require a reducible oxide support Montoya et al. used a Ce doped ZrO$_2$ support to show oxygen mobility at the metal-support interface to be crucial for a stable catalyst.\[6\] Odedairo et al. reported that a plasma treatment of Ni/CoO$_2$ enhances the metal-support interface and generates a clean metal surface, both effects leading to a higher activity in methane dry reforming.\[6\] Rezaei et al. have increased the metal support interface via synthesis of a high surface area CeO$_2$-ZrO$_2$.\[6\] In contrast, Iglésias et al. concludéd 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 CH$_4$ on the active metal is the rate determining step. Bitter et al. described a bifunctional mechanism for dry reforming of methane over Pt/ZrO$_2$ catalysts, where CH$_4$, is decomposed forming H$^+$ and CH$_4^*$ species on the metal surface, while CO$_2$ 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 O$_2$ 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 CO$_2$ through CO$_2$ induced nano-structuring of the Ni-ZrO$_2$ 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 O$_2$). The key to enable this concept is a reducible support that interacts moderately strong with CO$_2$, 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/ZrO$_2$ catalyst to CO$_2$ allows to maximize this interface and leads to a highly active catalyst. This will be combined with a periodic oxidative treatment in CO$_2$ for coke removal, which has no adverse effect on the activity of the catalyst compared to the regeneration in O$_2$. It has to be mentioned that this procedure has also an advantage from the point of operating the reaction on industrial scale. When using CO$_2$ regeneration can be initiated by removing CH$_4$ from the reactant gas (leaving the flow of CO$_2$) and after regeneration is completed the reaction can be started again by adding CH$_4$ to the reactant gas stream. This allows to avoid an additional purging of the reactor with inert gas, which is otherwise necessary if diluted O$_2$ 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 CH$_4$ conversion in DRM of Ni supported on SiO$_2$, Al$_2$O$_3$ and ZrO$_2$ 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
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 CH2 conversion reported in literature.[6] 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 restores 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 (a) Ni/ZrO2, (b) Ni/Al2O3, (c) Ni/SiO2 and (d) CO2 treated Ni/ZrO2 at 1073 K before reaction. The catalysts were treated with 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].](image)

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 Ni4+ 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 Ni was oxidized to Ni4+ 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 Ni/Al2O3 (Figure 2 C).

![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).](image)

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 enthalpies for different oxidation reactions of Ni and carbon.](image)

<table>
<thead>
<tr>
<th>Reaction Equation</th>
<th>Reaction Enthalpy</th>
<th>( \Delta H^\circ ) (kJ mol(^{-1}))</th>
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<tbody>
<tr>
<td>( \text{CO}_2 + \text{C} \rightarrow 2\text{CO} )</td>
<td></td>
<td>169.9</td>
</tr>
<tr>
<td>( \text{Ni} + \text{CO}_2 \rightarrow \text{NiO} + \text{CO} )</td>
<td></td>
<td>47.1</td>
</tr>
<tr>
<td>( \text{C} + \text{O}_2 \rightarrow \text{CO}_2 )</td>
<td></td>
<td>-394.8</td>
</tr>
<tr>
<td>( 2\text{Ni} + \text{O}_2 \rightarrow 2\text{NiO} )</td>
<td></td>
<td>-235.2</td>
</tr>
</tbody>
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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
The additional availability of oxygen atoms provided by ZrO₂ rate of Ni/ZrO₂ metal support interface aided the dissociation of CO₂ Hz were recorded during switching from He to CO. The rate of oxygen formation from CO₂ differed between Ni/SiO₂ and Ni/ZrO₂, thus we attribute the higher oxidation of Ni (k = 0.48 s⁻¹, grey dataset in Figure 4), which we assign to an increase in the interface between Ni and ZrO₂.

Exposure of Ni/ZrO₂ caused by saturation of the oxygen vacancies with oxygen from CO₂ led to a further enhancement of the rate of oxidation of Ni (k = 0.48 s⁻¹, grey dataset in Figure 4), which we assign to an increase in the interface between Ni and ZrO₂.

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. It has been paradigmatically stated in literature [13-16] 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. The shoulder observed above 2010 cm⁻¹ is attributed to CO adsorbed on partially oxidized Ni. 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, 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, and the bands below 2070 cm⁻¹ to CO adsorbed on isolated Ni atoms.
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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![Figure 6. Schematic representation of the elementary steps of CO\(_2\) treatment.](image-url)


The activity of Ni/ZrO$_2$ catalysts for dry reforming of methane is enhanced by activation and regeneration of the catalyst in presence of CO$_2$. In situ XAS and FTIR of adsorbed CO have shown that an increased metal support interface created during the CO$_2$ treatment opens an additional pathway for CO$_2$ activation providing labile oxygen species for carbon removal.