Structural response of Ni/ZrO$_2$ to feed modulations during CH$_4$ reforming reactions

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Abstract. Time resolved oxidation and reduction cycles of ZrO$_2$-supported Ni catalysts for dry reforming of CH$_4$ (CO$_2$ + CH$_4$ $\leftrightarrow$ 2 CO + 2 H$_2$) during feed modulations have been studied. Under reaction conditions (1073 K) Ni remains fully reduced, whereas switching the feed gas to pure CO$_2$ results in a slow (25 sec) formation of a stable NiO phase. When switching back to reaction conditions the NiO phase is rapidly reduced (~ 1 sec) to metallic Ni. In the context of this study, a novel capillary cell has been built, allowing the parallel treatment of 5 catalyst samples with different gas compositions and different pressures. A comparison of the capillary cell to conventional systems regarding the spectral quality and the kinetic data shows that the capillary cell can be used to obtain identical kinetic data and high quality X-ray absorption spectra.

1. Introduction

Dry reforming of CH$_4$ (CO$_2$ + CH$_4$ $\leftrightarrow$ 2 CO + 2 H$_2$) produces a synthesis gas with a H$_2$/CO ratio close to one. To reach acceptable conversion levels, reaction temperatures around 1000 K are required to shift the equilibrium to the side of the products. At this temperature metal sintering and agglomeration of the active phase play an important role. Since the usage of non-noble metals makes the process more economic, metals like Co or Ni were intensively studied in the last decades. Ni shows, in contrast to noble metals like Pt or Ir, a strong deactivation, that depending on the support can result from coking or metal sintering. Since coke deposited on the metal can be removed with gasifying agents such as O$_2$ or CO$_2$, cycle stability of the catalysts becomes an important issue for a successful catalyst development. Takenaka et al. [1] reported that gasifying deposited carbon over a SiO$_2$ supported Ni catalysts leads to a higher rate of particle agglomeration, since SiO$_2$ shows only weak metal-support interaction. Wei et al. [2] have shown that the initial activity of a modified Ni/ZrO$_2$ catalyst for CH$_4$ decomposition can be restored by gasifying the deposited carbon with CO$_2$. The periodic treatment of a Ni/ZrO$_2$ catalyst in CO$_2$ is also applicable for DRM, but there is no study on the influence of this treatment on the structural properties of the active metal published so far.

In this study the structural changes of Ni/ZrO$_2$ during cycles of CH$_4$ dry reforming and periodic gasification of the deposited carbon with CO$_2$ have been investigated. To effectively utilize the synchrotron radiation, a novel five-fold capillary cell has been developed, allowing the pretreatment of
five catalysts in parallel. This cell has been tested with respect to spectral quality and comparability of the kinetic data to a lab-scale reactor for dry reforming of CH₄.

2. Experimental

Ni supported on ZrO₂ (Mel chemicals, XZO1501/03) was prepared via incipient wetness impregnation of an aqueous solution of Ni (II) nitrate hexahydrate (Acros) as described previously.[3] After impregnation, the catalyst was dried over night at 373 K, calcined in air at 673 K for 2 h (flow rate: 100 mL·min⁻¹) and pre reduced in pure H₂ at 873 K for 12 h (heating rate 0.5 K·min⁻¹).

The activity tests were carried out in a 4 mm plug flow reactor made of quartz glass. The catalyst was fixed between two plugs of quartz wool. Prior to reaction at 1073 K the catalyst was reduced in situ at 873 K in 10 % H₂ in He for 90 minutes. The reaction was carried out at ambient pressure with a reactant gas consisting of 15 vol.% CH₄ (99.995 vol.%), 15 vol.% CO₂ (99.995 vol.%) and 70 vol.% He (99.999 vol.%) with a total flow of 80 mL·min⁻¹. The catalytic test in the capillary was carried out at identical conditions. To obtain the same space velocity the total flow was adjusted to 10 mL·min⁻¹. The product gas was analyzed with an online mass spectrometer (Pfeiffer Omistar GSD 320).

The X-ray absorption spectra were obtained at the SuperXAS beamline at the SLS synchrotron in Villigen, Switzerland. All data were recorded in transmission mode at the Ni K-edge at 8333 eV using a QEXAFS channel-cut Si(111) monochromator operated at an oscillation frequency of 2 Hz. All in situ X-ray absorption spectra were measured in a capillary made of quartz glass (1 mm diameter, 20 µm wall thickness, Hilgenberg), were the pressed catalyst was fixed with two plugs of quartz wool. After reduction at 873 K in 10 % H₂ in He for 90 minutes, the catalyst was heated to 1073 K in He with a hot air blower from below before exposing the catalyst to the reactant gas. After 10 minutes, the reactor was flushed with He before introducing CO₂ to the catalysts. The capillaries were sealed in a U-shaped sample holder allowing the parallel treatment of 5 samples (Figure 1).

Figure 1: 3D model of the in situ cell (a) and horizontal cut to see the gas supply lines (b), 1: holes for gas supply lines; 2: catalyst bed; 3: capillaries.

The capillaries were located in a vertical distance of 4 mm (center to center) and in a horizontal distance of 4.5 mm (Figure 1 a). For gas supply, 1/8” tubes were mounted at the outside of the cell (Figure 1 b). To compare the signal quality obtained from the capillaries to a conventional pellet cell, a self-supporting wafer of the 10 wt.% Ni/ZrO₂ catalyst was prepared and spectra were recorded before and after reduction in 10 % H₂ in He.
3. Results and discussion

3.1. Comparison of the capillary cell with conventional reactors with respect to XAS and kinetics

Figure 2 a) and b) show the $k^2$-weighted EXAFS obtained in a conventional pellet cell [4] in comparison to the capillary of 1 mm outer diameter. The EXAFS are identical up to $k = 9 \text{Å}^{-1}$, for higher values of $k$ the noise level in the capillary cell becomes higher.

Since operando studies should be carried out under identical conditions as the kinetic studies in the lab, reactions in a capillary should show the same rates compared to a lab-scale reactor. Figures 2 c) and d) show a comparison of the conversions obtained in a 1 mm capillary and in a 4 mm plug flow reactor used for kinetic studies of the dry reforming of CH$_4$ at the same space velocity. Both reactor types showed similar CO$_2$ and CH$_4$ conversion levels as well as equal H$_2$/CO ratios in the product gas, which proves that both reactors have an identical kinetic behaviour.

3.2. Structural changes of the Ni particles during feed modulations

The changes in the oxidation state of the Ni/ZrO$_2$ catalyst during feed modulations between 15 % CH$_4$, 15 % CO$_2$ in He (reactant gas for CH$_4$ DRM) and pure CO$_2$ are shown in Figure 3. After the reduction at 873 K and the subsequent heating in He to 1073 K the catalyst was fully reduced. During the following cycle in CO$_2$ atmosphere, Ni was completely oxidized to NiO in ~ 25 sec. During the first reaction cycle (shaded area in figure 3 b), NiO was reduced again to metallic Ni (~ 3 sec), consuming H$_2$ formed in the dry reforming reaction of CH$_4$. Please note that in contrast to Ni/SiO$_2$ [5], Ni/ZrO$_2$ shows no sintering after CO$_2$ treatment (observed from the EXAFS, data not shown), which can be attributed to the stronger metal-support interaction between Ni and ZrO$_2$. 

![Figure 2: k^2-weighted \(\chi(k)\) of an oxidized (a) and a reduced (b) 10 wt.% Ni/ZrO$_2$ catalyst obtained in a pellet cell (orange line) and in a capillary cell (1 mm, blue line) at room temperature and comparison of kinetic data obtained with a 2 wt.% Ni/ZrO$_2$ catalyst in a 1 mm capillary (c) and a 4 mm plug flow reactor (d); CH$_4$ conversion (blue dots), CO$_2$ conversion (orange squares) and H$_2$/CO ratio (red triangles).](image-url)
During the subsequent CO$_2$ treatment of the catalyst, deposited carbon was removed via the reverse Boudouard reaction (C + CO$_2$ $\leftrightarrow$ 2 CO, CO evolution detected via mass spectrometry, data not shown) and the Ni particles were oxidized to NiO. In the following reaction cycle, NiO was reduced to metallic Ni. Note that Ni shows the same degree of oxidation and the same coordination number after every cycle, which indicates that this procedure can be used to regenerate spent Ni catalysts, if the metal-support interaction is sufficiently strong to prevent agglomeration.

4. Conclusions
We have successfully shown the structural changes of a Ni/ZrO$_2$ catalyst during dynamic feed modulations using X-Ray absorption spectroscopy with very high time resolution. Switching the feed gas from dry reforming conditions (CH$_4$ + CO$_2$ in He) to pure CO$_2$ resulted in a slow oxidation (~ 25 sec) of the metallic Ni to NiO, whereas applying CH$_4$ and CO$_2$ resulted in a fast reduction of the NiO phase (~ 3 sec).

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