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Dynamic transformation of small Ni particles during methanation of CO₂ under fluctuating reaction conditions monitored by *operando* X-ray absorption spectroscopy

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Abstract. A 10 wt.-% Ni/Al₂O₃ catalyst with Ni particles of about 4 nm was prepared and applied in the methanation of CO₂ under dynamic reaction conditions. Fast phase transformations between metallic Ni, NiO and NiCO₃ were observed under changing reaction atmospheres using *operando* X-ray absorption spectroscopy (XAS). Removing H₂ from the feed gas and, thus, simulating a H₂ dropout during the methanation reaction led to oxidation of the active sites. The initial reduced state of the Ni particles could not be recovered under methanation atmosphere (H₂/CO₂ = 4); this was only possible with an effective reactivation step applying H₂ at increased temperatures. Furthermore, the cycling of the gas atmospheres resulted in a steady deactivation of the catalyst. *Operando* XAS is a powerful tool to monitor these changes and the behavior of the catalyst under working conditions to improve the understanding of the catalytic processes and deactivation phenomena.

1. Introduction

Triggered by the increasing importance of renewable energies e.g. from wind and solar plants long term energy storage becomes more and more important to balance the seasonal fluctuations in the power grid. A process which addresses this problem is the “power to gas” concept, in which CO₂ is hydrogenated with sustainable H₂ (e.g. from water splitting) according to the Sabatier reaction. The resulting synthetic natural gas is a diversely applicable energy carrier.[1]

Supported nickel catalysts are well-established in the methanation of CO₂ under stationary conditions.[2-4] However, the behavior and deactivation of the catalyst under dynamic conditions have not yet been studied in detail. For example, fast load changes will most probably occur under realistic conditions due to a fluctuating supply of renewable H₂. In previous studies we used *operando* X-ray absorption spectroscopy (XAS) to investigate the methanation of CO₂ under changing reaction atmospheres and observed a fast oxidation after removal of H₂ from the feed gas.[5] In this work we present an extended experiment revealing the effects of cycling and a reactivation step on the catalyst. In this study, a catalyst with more defined Ni nanoparticles supported on γ -Al₂O₃ was used.



2. Experimental

X-ray absorption spectroscopy experiments were conducted at the ANKA synchrotron radiation facility in Karlsruhe, Germany, (2.5 GeV ring, 100-150 mA) at the XAS beamline. The measurements were performed at the Ni K edge (8333 eV) in transmission mode using an X-ray beam of 1 mm in height and 7 mm in width. A time resolution of 90 s for X-ray absorption near edge structure (XANES) and 300 s for extended X-ray absorption fine structure (EXAFS) spectra was used. For the *operando* experiments a quartz glass capillary (1 mm diameter, 20 μm wall thickness) was filled with a sieved fraction of the catalyst powder (100-200 μm , diluted with $\gamma\text{-Al}_2\text{O}_3$ 1:1) to get a catalyst bed in 10 mm length. The capillary was heated to the desired temperatures of 30-500 $^\circ\text{C}$ (10 K/min) using an Oxford GSB-1300 hot air blower.[6] Individual mass flow controllers (Bronkhorst) were used for gas dosing and online gas analysis was conducted using a Pfeiffer Vacuum mass spectrometer (ThermoStar GSD 320 T1). Gas mixtures of 15 % H_2/He , 3.75 % CO_2/He and 15 % $\text{H}_2 + 3.75$ % CO_2/He with constant gas flow of 50 mL/min were used resulting in a weight hourly space velocity (WHSV) of 37 h^{-1} (concerning CO_2 flow and catalyst mass). Data analysis was performed using the Athena and Artemis software of the IFEFFIT package.[7] Spectra of Ni and NiO nanoparticles as well as bulk NiCO_3 were used as references for linear combination analysis (LCA).

3. Results and discussion

Homogeneous deposition-precipitation using urea as precipitating agent [8, 9] led to a 10 wt.-% Ni/ Al_2O_3 catalyst which was X-ray amorphous, i.e. it did not show any reflections of NiO or Ni after reduction but only the reflections of the Al_2O_3 support in X-ray diffraction. Evaluation of the scanning transmission electron microscopy (STEM) images resulted in a mean Ni particle size of 4 nm, a narrow size distribution (3.7 ± 1.2 nm) and a dispersion of 21 %. According to the small particle size, the coordination number obtained from the EXAFS was calculated as 6.1 ± 1.4 for the metallic Ni and is much lower compared to the coordination number in bulk Ni which is 12.0. The Ni-Ni bond distance of 2.46 \AA is shortened (2.49 \AA in bulk), showing a contraction of the bond length due to the smaller particle size. The specific surface area of the catalyst was $200 \text{ m}^2/\text{g}$. The catalyst was also tested in the laboratory with a comparable setup yielding in a turnover frequency (TOF) of 38 h^{-1} (measurements analogous to the previous work [5]) and CO as the only byproduct.

Figure 1(a) visualizes the results of the *operando* XAS experiment which was performed based on earlier works in our group.[5] The corresponding XANES spectra in each atmosphere at 400°C can be seen in Figure 2(a). A pre-reduced catalyst was activated in a flow of 15 % H_2/He at an oven temperature of 500°C (10 K/min, temperature $460\text{-}470^\circ\text{C}$ measured with a thermocouple at the location of the capillary) for about 40 min. Obviously, the catalyst was not fully reduced which might be due to the strong interaction of the small Ni particles with the Al_2O_3 support and the low H_2 concentration used for the activation. On the other hand, no NiAl_2O_4 spinel species could be identified in linear combination (LC) fitting. The capillary was cooled to room temperature to receive a spectrum of the reduced catalyst in good quality as reference.

Afterwards the gas atmosphere was switched to methanation conditions ($\text{H}_2/\text{CO}_2 = 4$, 81 % He) and the reactor was heated to 400°C (10 K/min, real temperature $350\text{-}360^\circ\text{C}$). Even at room temperature the catalyst was oxidized to some extent but was reduced again when the production of CH_4 started at about 200°C . 80 % of the Ni nanoparticles remained in the reduced state during the 40 min methanation period at 400°C . After removing H_2 from the gas stream 75 % of the Ni fraction were immediately oxidized in the less reducing atmosphere and the formation of CH_4 stopped as well in the absence of H_2 . After another 40 min, H_2 was introduced again to restore the previous methanation conditions. In the first few minutes Ni was reduced fast and afterwards more slowly resulting in about 50 % metallic Ni. The oxidation of the catalyst during the next switch to the less reducing atmosphere took longer than during the first switch. In the third and fourth methanation cycle a behavior similar to the second cycle was observed which means that the fast reduction in the first few minutes was decelerating over time.

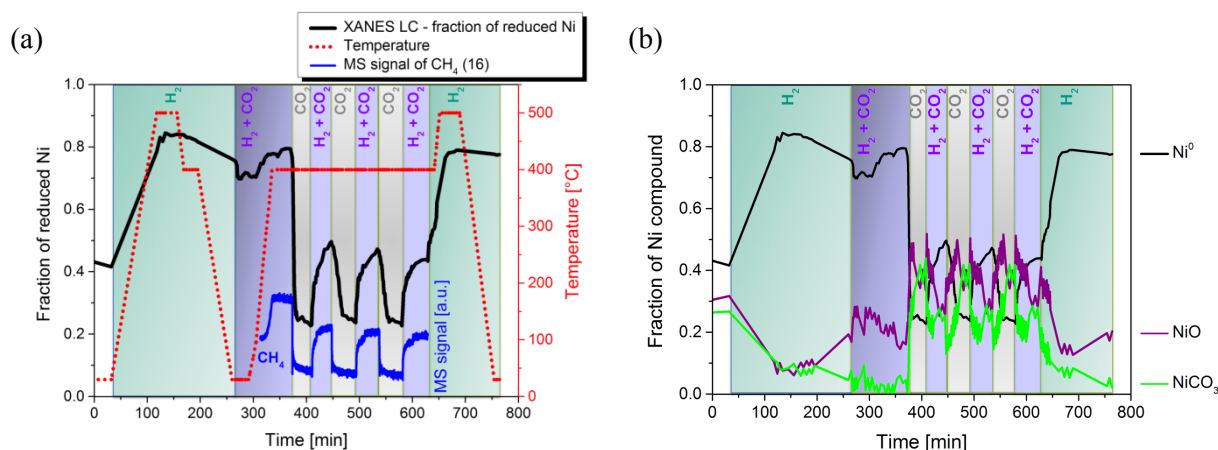


Figure 1. (a) *Operando* XAS experiment for the methanation of CO₂ with a 10 wt.-% Ni/Al₂O₃ catalyst at ANKA synchrotron Karlsruhe. The fraction of the Ni compounds was calculated using linear combination analysis (LCA) of the spectra. (b) Fraction of Ni, NiO and NiCO₃ during the experiment.

Overall, the maximum percentage of metallic Ni decreased with the number of cycles and also the produced amount of CH₄ decreased slightly. The first H₂ dropout caused a faster oxidation than the following cycles which might be due to oxygen contamination in the system. Therefore, a deep bulk oxidation occurred which was not fully reversible under methanation atmosphere. In the following cycles dynamic oxidation and reduction of the Ni particles with a small but continuous deactivation was observed.

Figure 1(b) shows the development of each Ni phase during the experiment calculated from linear combination analysis. After exposure to air the pre-reduced catalyst showed a Ni and NiO phase as well as NiCO₃ formation. After cooling to room temperature in H₂ atmosphere and the start of the methanation, NiO was formed and only traces of NiCO₃ were present in the catalyst. Removal of H₂ from the feed gas always led to the formation of NiO in the first step and its subsequent conversion into NiCO₃ (best seen in CO₂ cycle 2 and 3). In the following methanation atmosphere first a fast reduction of NiCO₃ occurred followed by a delayed slower reduction of NiO to metallic Ni. Roughly 30 % of each oxidized compound remained on the catalyst during the methanation sequences after the first H₂ dropout. In addition, a band around 1448 cm⁻¹ [10] in diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) experiments could be assigned to NiCO₃.

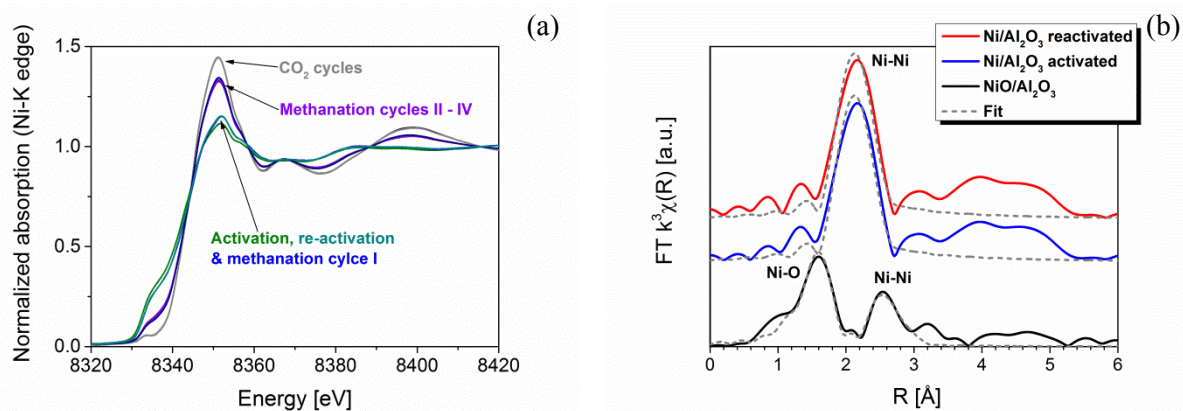


Figure 2. (a) Normalized XANES spectra at 400°C for each atmosphere according to Figure 1. (b) Magnitude of Fourier transformed k^3 -weighted EXAFS spectra recorded at room temperature along with the corresponding fits.

As a result of the Ni oxidation during H₂ dropout a reactivation step was conducted at the end of the experiment recovering the same fraction of reduced Ni (78 % at room temperature, see Figure 1(a)) as after the activation in the beginning. Furthermore, an increase in the production of CH₄ nearly to the initial yield was observed in laboratory experiments (not shown here). As depicted in Figure 1(b) bulk NiO and NiCO₃ could only be reduced in a reactivation step flushing the reactor with H₂ at 500 °C. A reactivation step with higher H₂ concentrations might be even more effective.

Comparing the EXAFS spectra of the activated catalyst and the catalyst after the reactivation step at room temperature (Figure 2(b)), no significant changes could be observed and the Ni coordination number was calculated to the similar value of 6.0±1.4, the same for the Ni-Ni bond distance of 2.46 Å. Therefore, it can be concluded that the size of the particles did not change during this short experiment. Repeating the experiment several times in the laboratory led to Ni particle sintering up to a mean diameter of 5 nm which was determined from STEM images. Thus, further studies on the dynamic behavior of supported nanoparticles under fluctuating reaction conditions are currently performed in our group.

4. Conclusion

A 10 % Ni/Al₂O₃ catalyst with an average particle size of 4 nm and a narrow size distribution was prepared and applied in the methanation of CO₂ (H₂/CO₂ = 4) under dynamic reaction conditions. In a less reducing atmosphere after H₂ dropout metallic Ni was oxidized to NiO and NiCO₃. Accordingly a slight but steady deactivation of the catalyst with each cycle was observed. After adding H₂ to restore methanation conditions, NiCO₃ was first converted to NiO which was then reduced to metallic Ni. However, the initial fraction of reduced Ni could not be reached. An effective reactivation step with H₂ at 500 °C was able to recover the initial state of the catalyst. This experiment illustrates that *operando* XAS is a powerful tool to analyze catalysts under working conditions and to monitor changes of the active centers. This is crucial for a better understanding of the catalytic processes and the reasons for deactivation, especially in the methanation of CO₂ under dynamic reaction conditions.

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