

In-situ PDF study on a $\text{La}_{0.5}\text{Ce}_{1.5}\text{NiO}_4$ perovskite-derived methanation catalyst under dynamic operation conditions

1. Abstract

With this proposal, we would like to study the structural changes of a $\text{La}_{0.5}\text{Ce}_{1.5}\text{NiO}_4$ perovskite-derived catalyst that occur during changing gas feed compositions in the methanation reaction. Our chosen conditions take into account the unsteady green hydrogen supply impinged by renewable energy. We synthesized an active catalyst by calcination of $\text{La}_{0.5}\text{Ce}_{1.5}\text{NiO}_4$ at 600 °C. The calcination process yields exposed NiO on the surface of the vacancy-rich perovskite, that acts as support. Catalytic experiments showed that the gas feed composition H_2/CO_2 has an influence on the activity and selectivity, as well as the longevity of the catalyst. With the here proposed pair distribution function (PDF) experiments we want to observe structural transformations of both, the active Ni phase, as well as the perovskite support structure. This includes changes of the oxygen vacancies, the sintering of nanoparticles (NP) and the evolution of the structural motifs and defects that enhance or suppress the activity or selectivity of the catalyst.

2. Scientific context

The use of renewable energies to replace fossil fuels needs storage concepts due to the natural fluctuations of renewable energy supply. The methanation of CO_2 using H_2 produced via electrolysis of water is an approach for long-term storage of energy from renewable resources. For the methanation reaction, catalysts are needed, that can resist a changing gas feed composition that occurs due to H_2 feed fluctuations. Common catalysts are Ni NP supported on Al_2O_3 . These are prone to deactivation due to sintering and oxidation during lower concentration of H_2 in the gas feed.^[1] Recently, A_2BO_4 type perovskites i.e. our $\text{La}_{2-x}\text{Ce}_x\text{NiO}_4$ -derived catalysts showed good performance in fluctuating feed mixtures.^[2] The $\text{La}_{0.5}\text{Ce}_{1.5}\text{NiO}_4$ -derived catalyst ($x = 1.5$) showed the highest activity, resistance to deactivation and the activity could be restored after several cycles of different H_2/CO_2 feed ratios (Fig. 1). From the characterization results of quasi in-situ XPS, STEM and CO pulse chemisorption the observed activity and stability during the CO_2 methanation can be attributed to tailored oxygen vacancies and good Ni dispersion in the $\text{La}_{0.5}\text{Ce}_{1.5}\text{NiO}_4$ derived catalyst. The average Ni particle size from STEM is 10.2 nm. Interestingly, the PXRD does not show reflections for Ni fcc (Fig. 2). We assume that La and Ce as heavy scatterers prevent Cu K α radiation from deeper penetration into the sample in Bragg Brentano geometry. Further, the scattering contrast of La/Ce compared to Ni (especially when NP are present) is too high to resolve with laboratory XRD. This, and the enhanced diffuse scattering from the most likely disordered Ni particles can explain the PXRD in Fig. 2. The different extraction paths of Ni from the perovskite structure can lead to such disorder during the reduction process. STEM proved a (111) faceting of the Ni NP. However, other active sites like step edge, corner, and terrace sites cannot be ruled out by STEM, whereas PDF coupled with e.g. RMC analysis can give insight to these differently coordinated sites,^[3] which can boost the catalytic performance. The PDF is able to detect small changes in the catalyst or the support structure by calculation of difference-PDFs (d-PDFs), when subtracting the unloaded support from the loaded catalyst sample. It is the aim of this proposal to exploit the high achievable time resolution of synchrotron high-energy total scattering data to follow in-situ the structural changes of the $\text{La}_{0.5}\text{Ce}_{1.5}\text{NiO}_4$ perovskite-derived catalyst, during the methanation reaction over several cycles under varying gas feed composition. Via PDF analysis we will track the formation of the active phase and investigate the oxygen vacancies and structural motifs during the dynamic reactions.

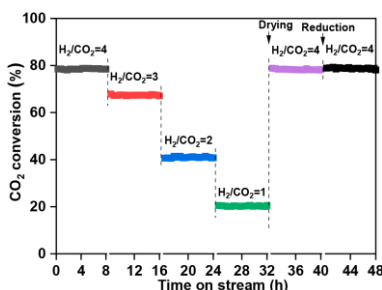


Fig. 2: CO_2 conversion of reduced $\text{La}_{0.5}\text{Ce}_{1.5}\text{NiO}_4$ under different H_2/CO_2 feed ratios.

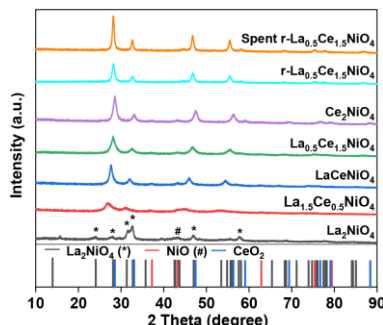


Fig. 1: PXRD of different $\text{La}_{2-x}\text{Ce}_x\text{NiO}_4$ catalysts and the reduced $\text{La}_{0.5}\text{Ce}_{1.5}\text{NiO}_4$ as well as the spent one.

Kommentiert [NP1]: Is this the case? Or are there only particles formed during the reduction with H_2 ?

Kommentiert [CA2R1]:
I am not sure about this, the NiO reduction degree was about 92% which means Ni(111) particles are the major component after reduction with H_2 .

Kommentiert [ZM3]: Is this proven or an assumption?

Kommentiert [CA4R3]:
It's mostly an assumption not directly proved, for the prepared samples we have seen a difference the reduction process via H_2 -TPR and we thought this can lead to structural disorder in the final catalyst.

3. Experiment proposed

High loadings of the heavy scatterers La and Ce make hard X-ray radiation indispensable. We apply for I15-1, perfectly suited for *in-situ* PDF experiments in the Q-range of 0.5 - 30 Å⁻¹ with a 65 keV X-ray beam using a small gold beamstop. We expect a time resolution of 1 min to be sufficient based on previous experiments. Data will be collected on the Perkin Elmer Detector.

Two catalysts (La_{0.5}Ce_{1.5}NiO₄ and Ni@La₂O₃-CeO₂) will be probed *in-situ*. A total gas flow of 20 mL/min will be used for all experiments, only gas compositions will be changed. PDF data will be collected continuously during the experiments. 20 mg of the catalyst powder will be placed inside a quartz capillary, fixed with glass wool. The capillary is connected via Swagelok connections to the gas inlet and outlet. Heating is provided by a resistive heater above and underneath the capillary for uniform heat distribution. Temperatures are measured inside the capillary with a thermocouple and gases are dosed with mass flow controllers. This equipment is brought by us. We further use a mass spectrometer to detect the reaction products, available from beamline I11, as inquired with Philip Chater.

The experiments consist of two essential steps: activation (reduction) and reaction. Activation is always the same to achieve comparable starting points for the catalysis, but the reaction conditions are altered.

Experiment I: After the sample is in place (takes 20 min), the flow cell is purged with inert gas (15 min). The gas is changed to pure H₂ and the temperature is then ramped up by 10 K/min to 600 °C (1 h) and the sample is reduced for 2 h. After reduction, the temperature is cooled down by 10 K/min to 350 °C (25 min) and the gas feed is changed to catalysis conditions (H₂/CO₂=4/1). Catalysis is done for 3 h to guarantee equilibrium and check the stability of the catalyst. The gas feed is then altered in the order 3/1, 2/1, 1/1 (Fig. 1), each at 350 °C and for 3 h. After the catalysis experiments, re-reduction will be done with pure H₂ at 600 °C (10 K/min) for 2 h. Afterwards, the sample is cooled down to 350 °C with 10K/min and gas feed is switched to catalysis conditions (H₂/CO₂ = 4/1) for 1 h (sums up to 20 h for this experiment).

We observed deactivation of the catalyst under pure CO₂. With **Experiment II**, we want to study the oxidation mechanism of pure CO₂ over the catalyst^[4], as well as the re-reducibility of the catalyst. The procedure for Experiment II is the same as in Experiment I, but instead of the first catalysis with (H₂/CO₂=4/1) we purge with CO₂ and skip the gas feed variations (sums up to 11 h).

Experiment I-II will also be done with the reference catalyst Ni/La₂O₃-CeO₂ which was synthesized via impregnation method (31 h). With this, we want to check which structural features of the perovskite-derived catalyst are responsible for the overall better performance. Setup, calibration and reference powder measurements of La₂NiO₄, Ce₂NiO₄, Ni@CeO₂, Ni@La₂O₃ take 10 h. Therefore, we apply for a total of 9 shifts (72 h) of beamtime.

4. Remote or mail-in options

Due to the complexity of the experiment there is no option to remotely control the experiment.

5. Results expected

To our knowledge, we propose the first *in-situ* PDF experiment on La_{2-x}Ce_xNiO₄ perovskite-derived catalysts to study their structural evolution during the dynamically operated methanation reaction. The catalyst is synthesized by the Palkovits Group (RWTH Aachen, Germany) and PDF analysis will be carried out by the Zobel Group (RWTH Aachen). We will get insight into the role of oxygen vacancies in the support, as well as the role of disorder in the active Ni phase. Extraction of these subtle changes will be done with difference-PDFs followed by a sophisticated refinement procedure with DiffPy-CMI and RMC, where needed. We will be able to see time-resolved changes in the catalyst during the methanation reaction. Finally, we will elucidate the structure-activity correlation of the catalyst, which will help future tailoring of this class of catalysts for the challenging conditions of methanation reaction with H₂ from renewable energies.

6. Publications

[1] Mutz et al., *Catalysts* **2017**, 7, 279.

[2] J. Ren et al., *Chem. Eng. J.* **2021**, 421, 131760.

[3] Quek et al., *Chem. Commun.*, **2014**, 50, 6005

[4] G. Giorgianni et al., *Phys.Chem.Chem.Phys.*, **2020**, 22, 18788.

Kommentiert [CA5]:

The PDF measurements will be:

1. Under inert conditions (calcined)
2. After reduction at 600 deg C and cool down to 350 deg C, before we start the reaction (before we introduce CO2 and H2)
3. Under reaction conditions (different reatio)
4. Re-reduction at 600 deg C and cooled down to 350 deg C.

Kommentiert [NP6]: Do we want to re reduce after the last step and check again the catalysis?

Kommentiert [r7R6]: Thank you for the suggestion. It is better to check the activity of the spent catalyst after the reaction. Actually, we also re-reduced the catalyst after the last step (H₂/CO=1/1), and then perform the methanation over the regenerated catalysts in the paper.

Kommentiert [CA8R6]:

I think re-reduction and measuring PDF is important but performing a reaction again will take too much time. In principle, it's enough to illustrate the dynamics under different conditions, calcined-reduced-under-reaction-re-reduced.

2 h re-reduction + 0.5 h for PDF measurement to check if the freshly reduced and the re-reduced after reaction are similar...

Kommentiert [NP9R6]: I would then still prefer to do 30 minutes catalysis after re-reduction instead of just measuring under H₂ gas (or just measure 1-2 min at 350°C). Keep in mind that 1-2 min is enough for a good PDF quality.

Kommentiert [CA10]:

The PDF measurements will be:

1. After reduction (reference PDF), this can be also a spectrum from experiment 1...
2. During CO₂ flow at 350 deg C
3. After CO₂ flow stopped
4. Re-reduction

Kommentiert [NP11]: It was impregnation wasn't it? Otherwise state the synthesis method.

Kommentiert [CA12R11]:

Yes, it's impregnation...