



Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal:
<https://www.esrf.fr/misapps/SMISWebClient/protected/welcome.do>

Deadlines for submission of Experimental Reports

Experimental reports must be submitted within the period of 3 months after the end of the experiment.

Experiment Report supporting a new proposal (“relevant report”)

If you are submitting a proposal for a new project, or to continue a project for which you have previously been allocated beam time, you must submit a report on each of your previous measurement(s):

- even on those carried out close to the proposal submission deadline (it can be a “*preliminary report*”),
- even for experiments whose scientific area is different from the scientific area of the new proposal,
- carried out on CRG beamlines.

You must then register the report(s) as “relevant report(s)” in the new application form for beam time.

Deadlines for submitting a report supporting a new proposal

- 1st March Proposal Round - **5th March**
- 10th September Proposal Round - **13th September**

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report in English.
- include the experiment number to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.



	Experiment title: Understanding the effects of manganese on reduction, reaction and dynamic behavior on catalytic activity of nickel-manganese spinel CO ₂ methanation catalysts	Experiment number: CH-6617
Beamline: BM31 (C04)	Date of experiment: from: 29.03.23 to: 03.04.23	Date of report: 24.11.23
Shifts: 12	Local contact(s): STOIAN Dragos Constantin, MARSHALL Kenneth	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): Tanja Franken*, Dennis Weber*, Friedrich-Alexander-Universität Erlangen-Nürnberg, Institute of Chemical Reaction Engineering, Group of Catalytic and Electrocatalytic Systems and Processes, 91058 Erlangen, Germany		

Report:

Introduction

Ni/Al₂O₃ is the state-of-the-art catalyst for the methanation of CO₂ due to the high selectivity and low cost of nickel. For this catalysts, sintering and oxidation of the nickel particles on the surface leads to a decrease in productivity with increasing time-on-stream, especially under dynamic H₂ dropout conditions.^{1,2} These dynamic H₂ dropout conditions arise from the fluctuation of renewable energies and the associated fluctuation of green hydrogen supply. Therefore, a catalyst is needed that can withstand these dynamic conditions and has high activity, selectivity, and stability. Spinel provides atomically distributed Ni with high stability, but this makes it difficult to activate. However, we show that spinel phases can be tailored to allow low-temperature activation, resulting in finely divided and highly active Ni sites.³ Furthermore, the redox reversibility of the spinel phase enables the reintegration and redispersion of the catalytically active Ni particles, thus reversing potential deactivation. This so-called concept of "Dynamic Responsive Methanation (DRM) Catalysts" is, with regard to the use of renewable energies for hydrogen production and the associated hydrogen dropouts, a possibility to utilize these dynamic operating conditions for reactivation of the catalyst.

Experimental procedure

Ni_{0.9}Mn_xAl_{2-x}O₄ (0 ≤ x ≤ 2) catalysts were prepared by coprecipitation of the corresponding nitrates with one molar sodium hydroxide at a constant pH of 9 and concurrent calcination at 800 °C. The supported NiMn₁/Al₂O₃ catalyst was prepared by incipient wetness impregnation and subsequent calcination at 500 °C. Ni & Mn K-edges were measured in the XANES (for Ni: 8270 – 8430 eV, Mn: 6500 – 6650 eV) or EXAFS (for Ni: 8230 – 9330 eV, Mn: 6440 – 7540 eV) range depending on the experiment. The XANES range is used to determine the oxidation states and can also be used with the linear combination analysis (LCA) to determine phase fractions based on reference samples. The EXAFS range will be used to determine bond lengths. In addition, XRD spectra (energy: 48.6 keV, wavelength: 0.25509 Å) were recorded to follow phase transitions during the experiments. The catalysts were tested using the quartz capillary flow reactor cells (1mm OD) and gas delivery systems available at the beamline. The corresponding spinel (Ni_{0.9}Al₂O₄, Ni_{0.9}Mn_{0.375}Al_{1.625}O₄ or Ni_{0.9}Mn_{1.75}Al_{0.25}O₄) or supported catalyst were diluted 1:3 with Quartz, pressed, crushed and the 50 – 100 μm fraction was filled into the capillaries. Depending on the experiment, the following procedures were used. The temperature programmed reductions (TPR) were conducted in 10% H₂ in He, with a heating ramp of 7.5 K/min up to 900°C. Pretreatment/Reduction of the catalyst was carried out by heating to 450 °C and holding for 1 h in 10 % H₂ in He. The *operando* CO₂ methanation experiments were performed at 350, 400 & 450 °C for 1h each with subsequent reoxidation at 500°C in synthetic air for 2h. Furthermore, the effect of H₂ dropouts were tested by switching off the H₂ supply several times for 1 h with subsequent methanation for 1 h.

Results

The XAS-TPR runs show that the introduction of manganese leads to the formation of active metallic Ni sites at lower temperatures. XRD-TPR confirmed that the $\text{Ni}_{0.9}\text{Mn}_{1.75}\text{Al}_{0.25}\text{O}_4$ spinel structure is destroyed during reduction from 400°C and a new $\text{Ni}_{0.25}\text{Mn}_{0.75}\text{O}_1$ phase is formed. In contrast in $\text{Ni}_{0.9}\text{Mn}_{0.375}\text{Al}_{1.625}\text{O}_4$ the supporting spinel structure stays intact. The H_2 dropout experiments revealed no change in oxidation state or activity for any of the catalysts tested.

The $\text{Ni}_{0.9}\text{Mn}_{0.375}\text{Al}_{1.625}\text{O}_4$ catalyst shows high redox cyclability, with Ni & Mn K-edges, phase fractions (LCA analysis of XANES data) and methane yields that remain unchanged after multiple consecutive cycles of active site formation by reduction and active site reintegration by oxidation into the hosting spinel structure (c.f. figure 1). This supports the possibility to reverse potential deactivation of the NiMnAl spinel catalyst.

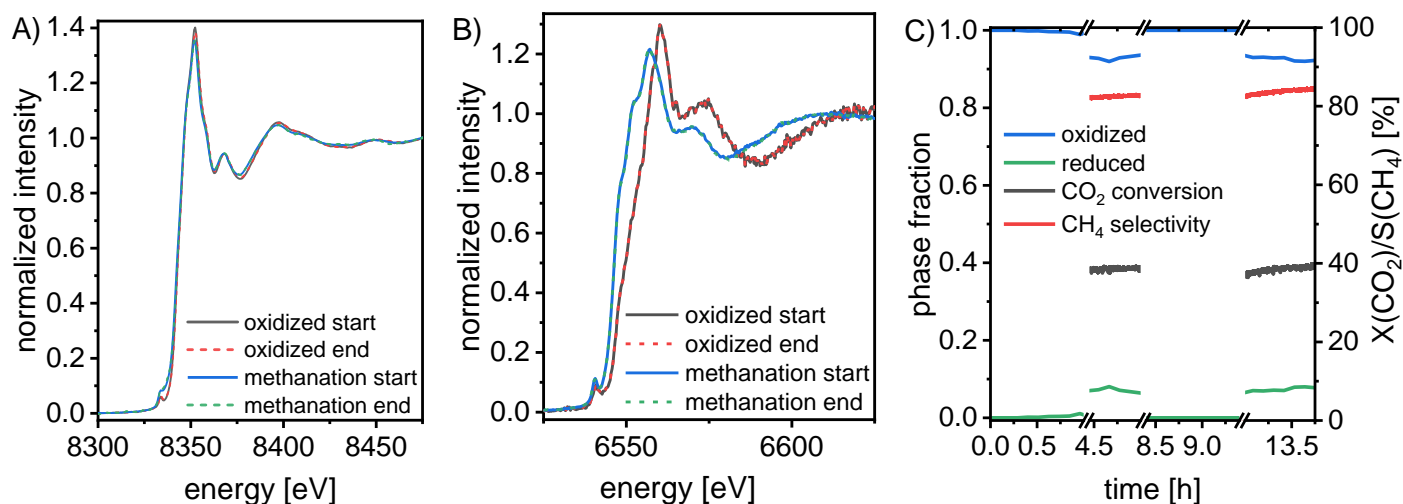


Figure 1: A) Ni K-edge & B) Mn K-edge of the oxidized and reduced $\text{Ni}_{0.9}\text{Mn}_{0.375}\text{Al}_{1.625}\text{O}_4$ catalyst before and after the redox cycle. C) Results of the LCA of the Ni-K edge and MS results for the *operando* CO_2 methanation experiment, showing the oxidized and reduced catalyst before and after the redox cycle. Reaction conditions: catalyst 1/3 diluted with quartz; $c(\text{CO}_2) = 6.25$ vol%; $c(\text{H}_2) = 25$ vol% in He; GHSV = 127270 h^{-1} ; atmospheric pressure; $T = 450^\circ\text{C}$.

The supported $\text{NiMn}_x/\text{Al}_2\text{O}_3$ and $\text{Ni}_{0.9}\text{Mn}_{1.75}\text{Al}_{0.25}\text{O}_4$ catalyst exhibits as expected low redox cyclability, with Ni & Mn K- edges, phase fractions and methane yields that no longer reach the origin after one additional reoxidation cycle (see Figure 2). These two sets of catalysts demonstrate our hypothesis, that a supporting stable spinel phase is necessary to allow for a dynamic creation and redispersion of active sites. In conventional supported systems this dynamic change is not possible. Based on these results two papers are in preparation.

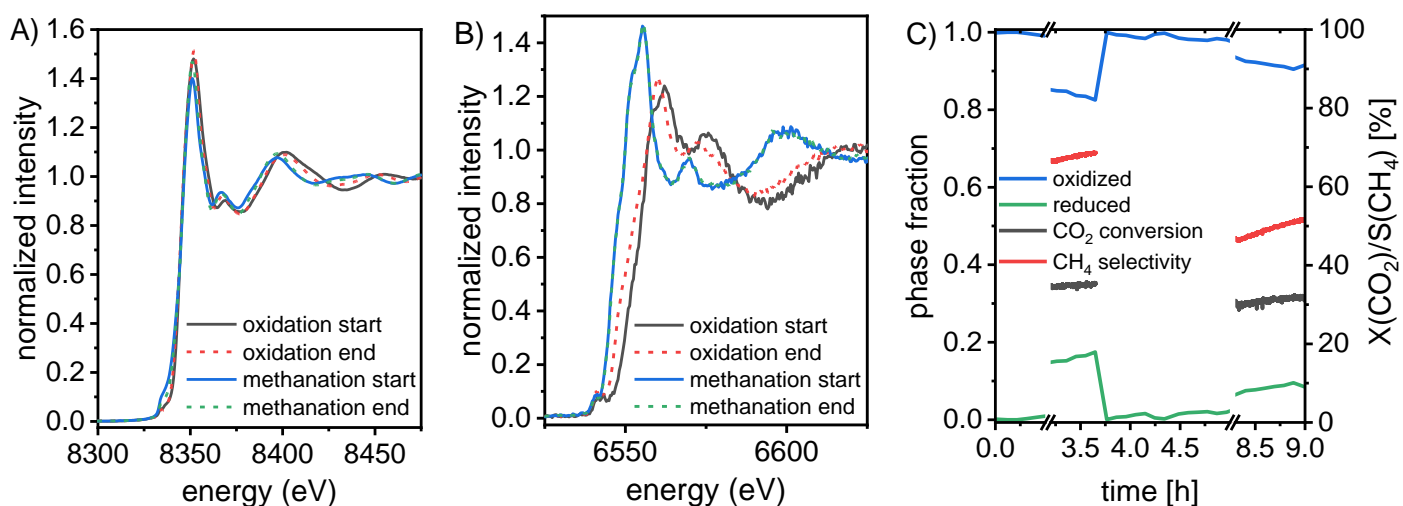


Figure 2: A) Ni K-edge & B) Mn K-edge of the oxidized and reduced $\text{NiMn}_1/\text{Al}_2\text{O}_3$ catalyst before and after the redox cycle. C) Results of the LCA of the Ni-K edge and MS results for the *operando* CO_2 methanation experiment, showing the oxidized and reduced catalyst before and after the redox cycle. Reaction conditions: see Fig 1.

References

- [1] Ewald, S. et al. *Applied Catalysis A: General* **2019**, 570, 376-386.
- [2] Mutz, B. et al. *Catalysts* **2017**, 7, 279.
- [3] Weber, D. et al. *ChemCatChem* **2022**, 14, e202200563.