



	<b>Experiment title:</b> Ni-Ga based catalysts for CO <sub>2</sub> hydrogenation to methanol: an operando pair distribution function analysis study	<b>Experiment number:</b> CH5884
<b>Beamline:</b>	<b>Date of experiment:</b> from: 04 May 2021 to: 09 May 2021	<b>Date of report:</b> 06 September 2023
<b>Shifts:</b> 12	<b>Local contact(s):</b> Stefano Checchia (stefano.checchia@esrf.fr)	<i>Received at ESRF:</i>
<b>Names and affiliations of applicants</b> (* indicates experimentalists): <b>Dr. Paula Macarena Abdala*<sup>†</sup>, Nora Zimmerli*<sup>†</sup>, Prof. Christoph Müller<sup>†</sup></b> <sup>†</sup> Laboratory of Energy Science and Engineering, Institute of Energy Technology, ETH Zurich, Leonhardstrasse 27, 8092 Zurich, Switzerland		

## Report:

**ABSTRACT:** Supported, bimetallic catalysts have shown great promise for the selective hydrogenation of CO<sub>2</sub> to methanol. In this study, we decipher the catalytically active structure of Ni-Ga-based catalysts for the hydrogenation of CO<sub>2</sub> to methanol. To this end, model Ni-Ga-based catalysts, with varying Ni:Ga ratios, were prepared by a surface organometallic chemistry approach. In situ differential pair distribution function (d-PDF) analysis revealed that catalyst activation in H<sub>2</sub> leads to the formation of nanoparticles of a Ni-Ga face-centered cubic (fcc) alloy and a small quantity of Ga which is not alloyed (GaO<sub>x</sub>). Structure refinements of the d-PDF data allowed to determine the amount of both Ga alloyed and GaO<sub>x</sub> species. In situ X-ray absorption spectroscopy experiments confirmed the presence of alloyed Ga and GaO<sub>x</sub> and indicated that upon alloying with Ga the electronic structure of Ni (viz. Ni<sup>δ-</sup>) is different to that of the pure metal. Both the Ni:Ga ratio in the alloy and the quantity of GaO<sub>x</sub> are found to be descriptors for methanol selectivity and methanol formation rate. The highest methanol selectivity and formation rate are associated with a Ni-Ga alloy with a Ni:Ga ratio of ~ 75:25 in combination with a small quantity of oxidized Ga species (0.14 mol<sub>GaO<sub>x</sub></sub> mol<sub>Ni</sub><sup>-1</sup>). Further, operando infrared spectroscopy experiments allowed us to hypothesize that GaO<sub>x</sub> species play a role in the stabilization of formate surface intermediates, which are subsequently further hydrogenated to methoxy species and ultimately to methanol. Our work demonstrates that the alloying of Ni with Ga is key to attain a high methanol selectivity (by minimizing CO and CH<sub>4</sub> formation) while oxidized Ga species enhance the rate of methanol formation.

## ABSTRACT REFERENCE:

Zimmerli, N. K.; Rochlitz, L.; Checchia, S.; Müller, C. R.; Copéret, C.; Abdala, P. Structure and Role of a Ga-Promoter in Ni-Based Catalysts for the Selective Hydrogenation of CO<sub>2</sub> to Methanol. ChemRxiv August 22, 2023. <https://doi.org/10.26434/chemrxiv-2023-4nfzt>