ESRF	**Experiment title:** Operando XAS-XRD study of Ni-Ga based intermetallic catalysts for CO_2 hydrogenation to methanol	**Experiment number**: CH6136
Beamline: BM31	**Date of experiment**: from: 22 September 2021 to: 28 September 2021	**Date of report**: 06 September 2023
Shifts: 18	**Local contact(s)**: Dragos constantin Stoian (dragos.stoian@esrf.fr) Wouter Van beek (wouter@esrf.fr)	*Received at ESRF:*

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Report:

ABSTRACT: Supported, bimetallic catalysts have shown great promise for the selective hydrogenation of CO_2 to methanol. In this study, we decipher the catalytically active structure of Ni-Ga-based catalysts for the hydrogenation of CO_2 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_2 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_x). Structure refinements of the d-PDF data allowed to determine the amount of both Ga alloyed and GaO_x species. In situ X-ray absorption spectroscopy experiments confirmed the presence of alloyed Ga and GaO_x and indicated that upon alloying with Ga the electronic structure of Ni (viz. $Ni^{\delta-}$) is different to that of the pure metal. Both the Ni:Ga ratio in the alloy and the quantity of GaO_x 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_{GaOx} mol_{Ni}^{-1}). Further, operando infrared spectroscopy experiments allowed us to hypothesize that GaO_x 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_4 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 CO2 to Methanol. ChemRxiv August 22, 2023. https://doi.org/10.26434/chemrxiv-2023-4nfzt