# Tracking the Phase Changes in Micelle-Based

# NiGa Nanocatalysts for Methanol Synthesis

# under Activation and Working Conditions

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Against the background of dwindling fossil fuel resources and the threats of climate change, sustainable and environmentally friendly production processes for fuels and chemical feedstock become all the more important. Methanol, a liquid fuel of high energy density, may contribute to pawing the way towards sustainable society [1]. It can be produced from green H2 generated via electrochemical water-splitting using solar or wind power, and the greenhouse gas CO2, extracted from air or already available concentrated at industrial sites [1]. In today’s catalysis industry, the synthesis of methanol is carried out from a mixture of H2, CO and CO2 over Cu/ZnO/Al2O3 catalysts, where high gas pressures (50 -100 bar) are required [2]. This traditional high pressure methanol synthesis does not only bring along safety risks and a high energy consumption, but restricts the CO2 concentration to a maximum of about 10% of the gas feed, since greater amounts result in a reduced methanol selectivity [6]. Accordingly, safe and energy-saving low pressure pathways for the methanol production using a higher percentage of CO2 in the feed are highly desirable.

Recently, intermetallic compounds, including NiGa alloys, have attracted attention as novel catalyst materials of improved stability, selectivity and activity for CO2 hydrogenation into methanol already at ambient pressure [3-6]. However, the underlying reaction mechanisms for CO2 hydrogenation and the nature of the active species in the NiGa system are still unclear. Accordingly, *in-situ* and *operando* studies on well-defined NiGa nanocatalysts are required.

In this work, we use a multi-probe approach combining *operando* X-ray absorption spectroscopy, *operando* powder X-ray diffraction and near-ambient pressure X-ray photoelectron spectroscopy with reactivity studies and ex situ microscopy techniques to shed light on the phase transitions and chemical compositions of SiO2-supported micelle-based Ni5Ga3 and Ni3Ga1 nanoparticles under activation (in H2) and reaction conditions for methanol synthesis (in CO2 and H2 mixture). This allows a direct correlation of the catalytic performance with the changes in structure, chemical state and surface composition of the catalysts, which will pave the way for an atomic-scale understanding of the hydrogenation of CO2 into methanol at ambient pressure.

References

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