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# Ni-Ga intermetallic compounds as novel catalysts for $CO_2$ hydrogenation to methanol

Irek Sharafutdinov[1], Christian Fink Elkjær[1], Christian D. Damsgaard[2], Diego Gardini[2], Felix Studt[3], Frank Abild-Pedersen[3], J. K. Nørskov[3], Søren Dahl[1]

[1]Department of Physics Building 307, Technical University of Denmark, DK-2800 Lyngby, Denmark
[2]Center for Electron Nanoscopy, Technical University of Denmark, DK-2800 Lyngby, Denmark
[3]SUNCAT Center for Interface Science and Catalysis, SLAC National Accelerator Laboratory, 2575 Sand Hill Road, Menlo Park, California 94025, USA and Department of Chemical Engineering, Stanford University, Stanford, CA 94305, USA

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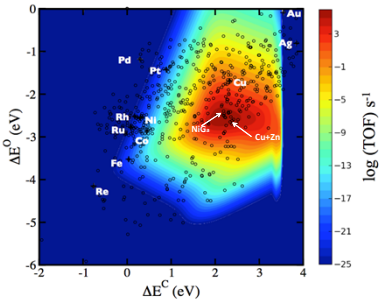
## Introduction and motivation

Synthesis of methanol from syngas (a mixture of carbon monoxide and hydrogen with small amounts of carbon dioxide) in an industrial scale is carried out at elevated temperatures and pressures (up to 250ºC and 60 bar respectively), which requires high operational and investment costs.

Synthesis of methanol from synthesis gas at lower temperature and pressure are desirable if methanol is to be synthesized as a sustainable fuel in decentralized units following biomass gasification or synthesis gas production by electrolysis.

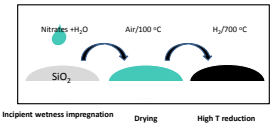
DFT enables computational indentification of potential catalysts for methanol synthesis based on the optimal binding energies of the intermediate species to the surface. In the present case, binding energies of carbon and oxygen were used as descriptors.

## DFT (Density Functional Theory) calculations

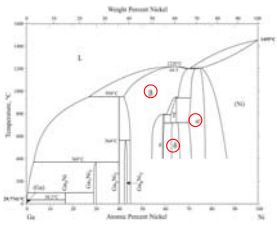


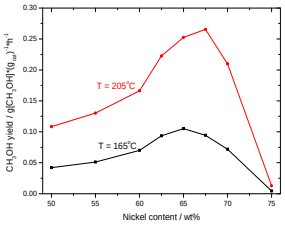

## Catalyst preparation

- A mixed aqueous solution of nickel and gallium nitrates was impregnated on high surface area silica (incipient wetness impregnation)
- Precursor dried and aged in air for 24 hours at 100-120ºC
- Reduced in pure hydrogen flow for 2 hours at 700ºC to form the Ni-Ga alloy.
- For comparison, a conventional $Cu/ZnO/Al_2O_3$ catalyst was synthesised following optimized co-precipitation method [1].



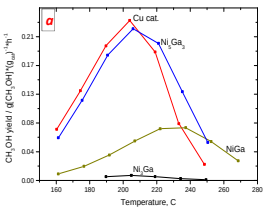

## Identifying optimal Ni/Ga ratio in the alloy

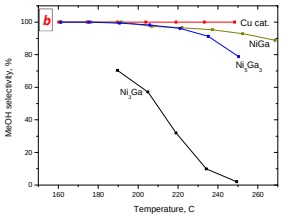


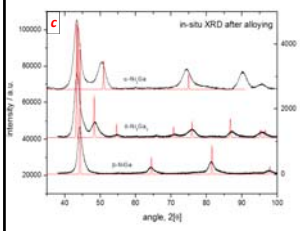



- A range of alloys with varying Ni/Ga ratio was prepared (metal loading: 17 wt%)
- Reaction conditions: 25% $CO_2$ and 75% $H_2$, P = 1 bar
- Activity measurements revealed maximum $CH_3OH$ yield corresponding to δ-phase (Ni ≈ 62÷ 68 mol. %)
- Ex-situ X-Ray Diffraction showed that α`, β, and δ phases were formed, corresponding to Ni/Ga ratio in the impregnation mixture (Ni-Ga phase diagram taken from [2])

## Further insight into $SiO_2$-supported β-NiGa, δ-$Ni_5Ga_3$ and α`-$Ni_3Ga$ catalysts

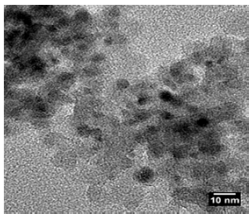


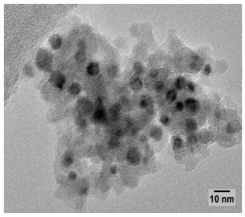




- At atmospheric pressure *(a)*, methanol yield from $Ni_5Ga_3/SiO_2$ system is comparable to a $Cu/ZnO/Al_2O_3$ catalyst
- $Ni_5Ga_3$ composition is close to the optimal in terms of activity
- High quality XRD scans *(c)* confirmed the formation of targeted phases [3]
- X-Ray Fluorescence confirmed adequate Ni/Ga ratio both before and after reduction/reaction cycle

## Transmission Electron Microscopy analysis



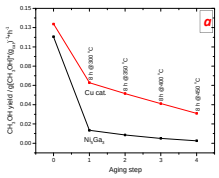

$Ni_5Ga_3/SiO_2$, d = 5.1 ± 1.2 nm

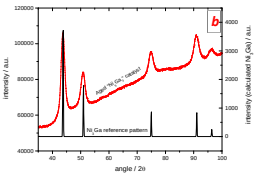



$NiGa/SiO_2$, d = 6.2 ± 1.7 nm

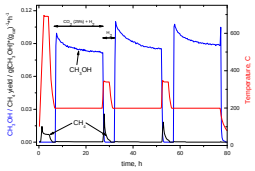
- Ni-Ga intermetallic nanoparticles with narrow size distribution were formed (post-run analysis)
- Complementary to XRF data, Energy Dispersive Spectroscopy both on single particle and large area confirmed that correct Ni/Ga ratio was achieved

## Stability of the $Ni_5Ga_3/SiO_2$ catalyst




- Stability test *in a fixed bed reactor* ***(a)*** consisted of several activity testing/aging cycles. Aging temperature was increased from 300ºC to 450ºC with steps of 50ºC. The gas mixture employed was 25% $CO_2$ and 75% $H_2$. Activity was measured at 180ºC after each aging step
- $Ni_5Ga_3$ phase transformed into $Ni_3Ga$ due to de-alloying ***(b)*** at high temperatures under reaction conditions




- Catalyst is deactivated under reaction conditions but fully regenerated at 350ºC in pure $H_2$ flow
- The activation energy for methane formation during regeneration ($E_A$ = 64,7 kJ/mol) correlates with α-carbon hydrogenation [4] (atomic carbon formed due to CO dissociation, $E_A$ = 70 kJ/mol)

## References

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