Ni-Ga intermetallic compounds as novel catalysts for CO2 hydrogenation to methanol

Sharafutdinov, Irek; Elkjær, Christian Fink; Damsgaard, Christian Danvad; Gardini, Diego; Studt, Felix; Abild-Pedersen, Frank; Nørskov, Jens Kehlet; Dahl, Søren

Publication date:
2012

Document Version
Publisher's PDF, also known as Version of record

CASE

Catalysis for Sustainable Energy

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

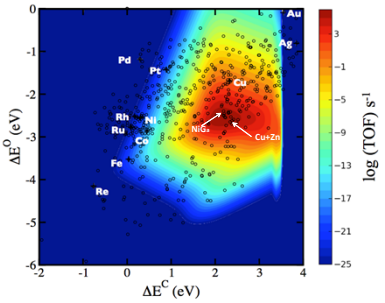
Introduction and motivation

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.

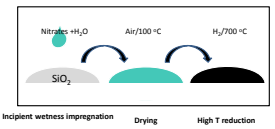
DFT enables computational indentification of potential catalysts for methanol synthesis based on the optimal binding energies of the intermediate species to the surface. In the present case, binding energies of carbon and oxygen were used as descriptors.

DFT (Density Functional Theory) calculations

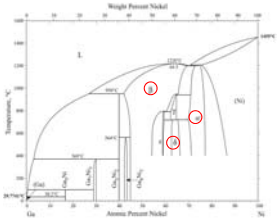


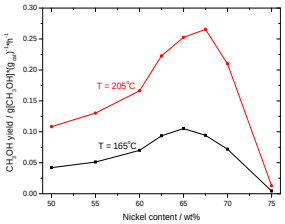
Catalyst preparation

- 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].



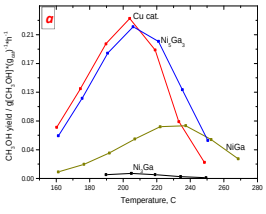
Identifying optimal Ni/Ga ratio in the alloy

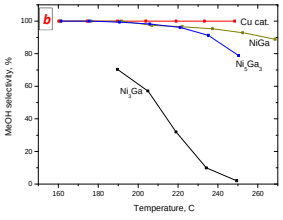


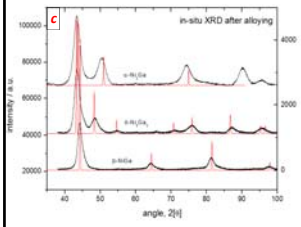


- A range of alloys with varying Ni/Ga ratio was prepared (metal loading: 17 wt%)
- Reaction conditions: 25% CO_2 and 75% H_2, P = 1 bar
- Activity measurements revealed maximum CH_3OH yield corresponding to δ-phase (Ni ≈ 62÷ 68 mol. %)
- Ex-situ X-Ray Diffraction showed that α`, β, and δ phases were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

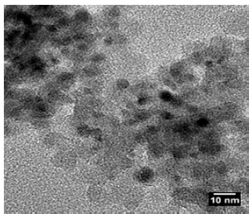




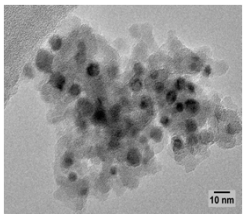


- At atmospheric pressure ***(a)***, methanol yield from Ni_5Ga_3/SiO_2 system is comparable to a $Cu/ZnO/Al_2O_3$ catalyst
- Ni_5Ga_3 composition is close to the optimal in terms of activity
- High quality XRD scans ***(c)*** confirmed the formation of targeted phases [3]
- X-Ray Fluorescence confirmed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

Transmission Electron Microscopy analysis



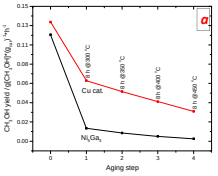
Ni_5Ga_3/SiO_2, d = 5.1 ± 1.2 nm

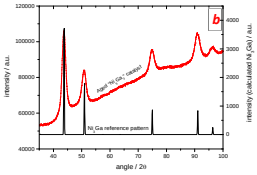


NiGa/SiO_2, d = 6.2 ± 1.7 nm

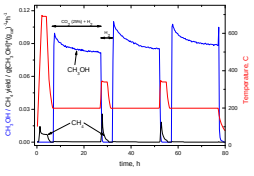
- Ni-Ga intermetallic nanoparticles with narrow size distribution were formed (post-run analysis)
- Complementary to XRF data, Energy Dispersive Spectroscopy both on single particle and large area confirmed that correct Ni/Ga ratio was achieved

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

[1] – C. Baltes, Journal of Catalysis, 258, 334-344 (2008)
[2] - H. Okamoto, Journal of Phase Equilibria and Diffusion, 31, 6, 575-576 (2010)
[3] - Inorganic Crystal Structure Database (http://www.fiz-karlsruhe.de/icsd.html)
[4] – C. Bartholomew, Applied catalysis A: General 212, 17-60 (2001)

Acknowledgements
This research was supported by the Office of Science of the U.S. Department of Energy through the SUNCAT Center for Interface Science and Catalysis at SLAC/Stanford, from the Danish Ministry of Science and Innovation through the Catalysis for Sustainable Energy Initiative (CASE) at DTU and by The Danish National Research Foundation through CINF DTU.
The A. P. Møller and Chastine Mc-Kinney Møller Foundation is gratefully acknowledged for its contribution towards the establishment of the Center for Electron Nanoscopy in the Technical University of Denmark.