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

Sharafutdinov, Irek; Elkjær, Christian Fink; Damsgaard, Christian Dan vad; 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

Citation (APA):
Ni-Ga intermetallic compounds as novel catalysts for CO₂ hydrogenation to methanol

**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 temperature and pressure to form methanol. Synthesis of methanol from CO₂ gas at lower temperature and pressure are desirable. The reaction can be simplified by electrolysis.

**DFT (Density Functional Theory) calculations**

A range of alloys with varying Ni/Ga ratio were prepared (metal loading: 17 wt%). Reaction conditions: 25% CO₂ and 75% H₂. P = 1 bar. Activity measurements revealed maximum CH₃OH yield at 450°C. Ni₅Ga₃ phase transformed into Ni₃Ga due to de-alloying.

**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% CO₂ and 75% H₂. P = 1 bar
• Activity measurements revealed maximum CH₃OH yield at 450°C (Ni₅Ga₃ phase)
• X-ray XRD Diffraction showed that X, β, and E phases were formed, corresponding to Ni/Ga ratio in the impregnation mixture (Ni-Ga phase diagram taken from [2])

**Further insight into SiO₂-supported B-NiGa, α-Ni₃Ga, and α-Ni₅Ga catalysts**

• At atmospheric pressure, CH₃OH yield from Ni₅Ga/SiO₂ system is comparable to a Cu²⁺/ZnO/NiO catalyst
• Ni₅Ga composition is close to the optimal in terms of activity
• High quality XRD score confirmed the formation of targeted phases
• X-Ray Fluorescence confirmed adequate Ni/Ga ratio both before and after reduction/reaction cycle

**Transmission Electron Microscopy analysis**

Ni₅Ga/SiO₂, d = 5.1 ± 0.2 nm
Ni₃Ga/SiO₂, d = 6.2 ± 1.7 nm

• Ni-Ga intermetallic nanocatalysts with narrow size distribution were formed (post-growth analysis)
• Complementary to XRD data, Energy Dispersive Spectroscopy (EDS) analysis of single particles and large area confirmed that correct Ni/Ga ratio was achieved

**Stability of the Ni₅Ga/SiO₂ catalyst**

• Stability test in a fixed bed reactor consisted of several activity testing/aging cycles. Aging temperature was increased from 300°C to 450°C with steps of 50°C. The gas mixture employed was 25% CO₂ and 75% H₂. Activity was measured at 300°C after each aging step.
• Ni₅Ga phase transformed into Ni₃Ga due to de-alloying Ni at high temperatures under reaction conditions
• Catalyst is deactivated under reaction conditions but fully regenerated at 300°C in pure H₂ flow
• The activation energy for methane formation during regeneration (Eₐ ~ 64 kJ/mol) correlates with a-catalyst hydrogenation (CH (gaseous carbon formed during CO₂ dissociation, Lₚ > 70 kJ/mol)

**References**


**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.