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

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**CASE**

**Catalysis for Sustainable Energy**


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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 is performed on industrial scale at elevated temperatures and pressures up to 250\degree C and 60 bar respectively, which requires high operational and investment costs.

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

**DFT (Density Functional Theory) calculations**

- 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 100-120\degree C.
- Reduced in pure hydrogen flow for 2 hours at 700\degree C to form the Ni-Ga alloy.
- For comparison, a conventional Cu/ZnO/Al\textsubscript{2}O\textsubscript{3} catalyst was synthesized following optimised co-precipitation method [1].

**Transmission Electron Microscopy analysis**

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

**Stability of the Ni\textsubscript{5}Ga\textsubscript{3}/SiO\textsubscript{2} catalyst**

- Stability test in a fixed bed reactor consisted of several activity testing/aging cycles. Aging temperature was increased from 300\degree C to 450\degree C with steps of 50\degree C. The gas mixture employed was 25% CO\textsubscript{2} and 75% H\textsubscript{2}.
- Activity was measured at 388\degree C after each aging step.

**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\textsubscript{2} and 75% H\textsubscript{2}, P = 1 bar.
- Activity measurements revealed maximum CH\textsubscript{3}OH yield for Ni/Ga ratio of 1.7.
- Ex-situ X-Ray Diffraction showed that \(\alpha\), \(\beta\), and \(\gamma\) phases were formed, corresponding to Ni/Ga ratio in the impregnation mixture (Ni-Ga phase diagram taken from [2]).

**Further insight into SiO\textsubscript{2}-supported \(\beta\)-NiGa, \(\delta\)-NiG\textsubscript{3}A, and \(\alpha\)-Ni\textsubscript{5}Ga catalysts**

- At atmospheric pressure (1atm), methanol yield from Ni\textsubscript{5}Ga\textsubscript{3}/SiO\textsubscript{2} system is comparable to a Cu/ZnO/Al\textsubscript{2}O\textsubscript{3} catalyst.
- Ni\textsubscript{5}Ga\textsubscript{3} composition is close to the optimal in terms of activity.
- High-quality XRD data confirmed the formation of targeted phases [2].
- X-Ray Fluorescence confirmed adequate Ni/Ga ratio both before and after reduction/reaction cycle.

**References**


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