Investigations into Ni$_5$Ga$_3$/SiO$_2$ intermetallic catalysts for CO$_2$ hydrogenation: synthesis and characterization

Sharafutdinov, Irek; Elkjær, Christian Fink; Damsgaard, Christian Danvad; Gardini, Diego; Chiarello, Gian-Luca; Wallace, Pereira de Carvalho Hudson; Grundwaldt, Jan-Dierk

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Motivation

- Recently, an increasing attention has been drawn towards the utilization of alloys and intermetallic compounds for catalytic purposes: in the number of applications, they represent attractive alternatives to conventional catalysts in terms of cost, activity, stability, and selectivity. In fuel cell applications, Pt- and alloy-based catalysts have been shown to possess enhanced activity compared to pure Pt [1]. For the selective semi-hydrogenation of acetylene to ethylene, Pt-Na intermetallic catalysts were found to be more selective and resistant to coking compared to industrially used Pt-Na [2]. Another example is Pt-Ni intermetallic compound, used in the anode side of the formic acid fuel cells: it is believed to have superior activity and CO tolerance, which has been previously shown to be active and selective towards CO₂ hydrogenation to form CH₃OH, can be prepared following simple impregnation method.

- However, despite the existence of a huge variety of intermetallic phases, a major challenge is to prepare well-defined supported nanoparticles in a sustainable and reproducible way [4]. Here we show that supported NiGa and Ni₅Ga₃ catalysts, with purposes: in the number of applications, they represent attractive alternatives to conventional catalysts in terms of cost, activity, stability, and selectivity. NiGa is observed.
- \( \alpha \)-NiGa formation is a more complex process; alloying starts with \( \delta \)-NiGa phase formation. At 500°C, \( \delta \)-NiGa is prevailing. Further, a mixture of \( \delta \)-NiGa, \( \psi \)-NiGa and \( \beta \)-NiGa phases is observed.

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 100-120°C.
- Reduced in pure hydrogen flow for 2 hours at 700°C to form the Ni-Ga alloy.

*In-situ Temperature Programmed Reduction & X-ray Diffraction of NiGa/SiO₂ and Ni-Ga₃ catalysts*

Experimental design: catalyst precursor is subjected to TPR in 50% H₂/He mixture. XRD scans are recorded at constant temperatures (high-quality 2-hour scans)

* Formation of an intermetallic phase from NiGa₃ precursor: in situ X-ray Absorption Spectroscopy

- Both nickel and gallium local structures start to change close to 500°C (compare with in-situ XRD spectra and Rietveld Refinement above).
- Nickel and gallium are reduced almost simultaneously.

* Proposed mechanism of alloying

- Nickel and gallium nitrates are decomposed to oxides.
- Reduction of gallium is slightly delayed.
- Ni is reduced to nickel.
- Ga₂O₃ is immediately reduced and alloyed on the nickel surface to form Ni-Ga.
- As temperature is increased, gallium oxide is further reduced and incorporated into the structure of intermetallic compound.

*References*