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CASE

Catalysis for Sustainable Energy

Investigations into Ni_5Ga_3/SiO_2 intermetallic catalysts for CO_2 hydrogenation: synthesis and characterization



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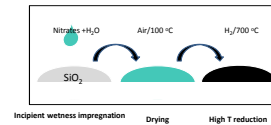
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Motivation

- 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 the fuel cells applications, Pt-Y alloy based catalysts were shown to possess enhanced activity compared to pure Pt [1]. For the selective semi-hydrogenation of acetylene to ethylene, Pd-Ga intermetallic catalysts were found to be more selective and resistant to coking compared to industrially used Pd-Ag [2]. Another example is Pt-Bi intermetallic compound, used in the anode side of the formic acid fuel cells: it is believed to have superior activity and CO tolerance with respect to pure platinum [3].
- 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 Ni_5Ga_3 catalysts, which have been previously shown to be active and selective towards CO_2 hydrogenation to form CH_3OH , can be prepared following simple impregnation method.

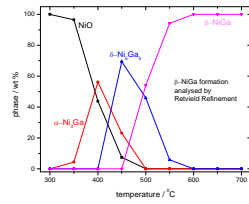
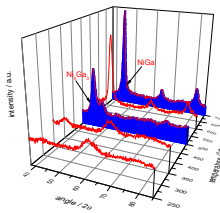
Catalyst preparation

- 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.

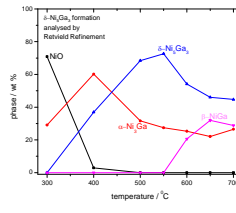
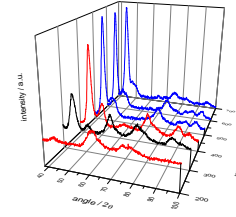


In-situ Temperature Programmed Reduction & X-ray Diffraction of $NiGa/SiO_2$ and Ni_5Ga_3 catalysts

Experimental design: catalyst precursor is subjected to TPR in 90% H_2/He mixture. XRD scans are recorded at constant temperatures (high quality 2 hour scans)

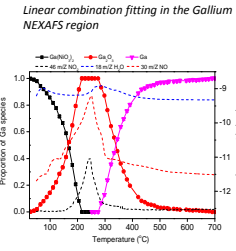
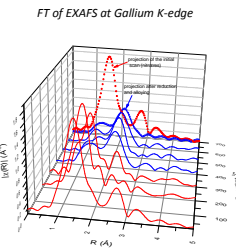
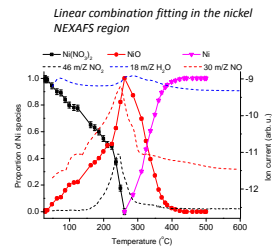
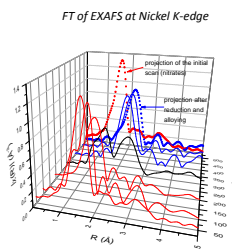


- β -NiGa phase formation proceeds through intermediate δ - Ni_5Ga_3 and α - Ni_3Ga [5,6] formation at 500°C. At 600°C, complete transformation into β -NiGa is observed.
- Alloying proceeds through more Ni-rich phases



- δ - Ni_5Ga_3 formation is a more complex process; alloying starts with α - Ni_3Ga phase formation. At 500°C, δ - Ni_5Ga_3 is prevailing. Further, a mixture of δ - Ni_5Ga_3 , α - Ni_3Ga and β -NiGa phases is observed

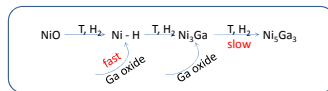
Formation of an intermetallic phase from Ni_5Ga_3 precursor: in situ X-ray Absorption Spectroscopy



- Both nickel and gallium local structure starts to change close to 300°C (compare with in-situ XRD spectra and Retveld 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:
 - NiO is reduced to nickel
 - Ga_2O_3 is immediately reduced and alloyed on the nickel surface to form Ni_3Ga
- As temperature is increased, gallium oxide is further reduced and incorporated into the structure of intermetallic compound



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