Optimizing Ni-Fe-Ga alloys into Ni\textsubscript{2}FeGa for the hydrogenation of CO\textsubscript{2} into methanol

Smitshuysen, Thomas E.L.; Nielsen, Monia R.; Pruessmann, Tim; Zimina, Anna; Sheppard, Thomas L.; Grunwaldt, Jan-Dierk; Chorkendorff, Ib; Damsgaard, Christian D.

Published in:
ChemCatChem

Link to article, DOI:
10.1002/cctc.202000174

Publication date:
2020

Document Version
Peer reviewed version

Link back to DTU Orbit

Citation (APA):

General rights
Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.
Optimizing Ni-Fe-Ga alloys into Ni$_2$FeGa for the hydrogenation of CO$_2$ into methanol

Thomas E. L. Smithhuysen$^{[a]}$, Monia R. Nielsen$^{[b]}$, Tim Prueßmann$^{[c,d]}$, Anna Zimina$^{[c,d]}$, Thomas L. Sheppard$^{[c,d]}$, Jan-Dierk Grunwaldt$^{[c,d]}$, Ib Chorkendorff$^{[a]}$, Christian D. Damsgaard$^{[a,b]}$

Abstract: A screening study of the catalytic performance of ternary alloy nanoparticles containing nickel, iron and gallium supported on silica for methanol synthesis from CO$_2$ and H$_2$ was performed. Catalysts were prepared by incipient wetness impregnation and subsequently reduced in H$_2$ before catalytic testing. Ni$_2$FeGa showed the best performance of the tested catalysts in terms of methanol yield. An optimization of the preparation was done to improve activity and selectivity, reaching performance close to that of prepared commercially available Cu/ZnO/Al$_2$O$_3$/MgO at low reaction temperatures and pressure. Extensive in situ characterisation using environmental TEM, in situ XRD and in situ EXAFS of the formation of the Ni$_2$FeGa catalyst explains an optimal reduction temperature of 550°C: warm enough that the three atomic species will form an alloy while cold enough to prevent the catalyst from sintering during the formation.

Introduction

Human energy consumption is both a current and urgent issue, due to its direct relation towards increased financial needs and the impact on nature as a whole, for example the current prevalence of fossil-based carbon feedstock beings an anthropogenic source of global warming. The present problem of having an energy infrastructure mainly running on carbon-fuels could be mitigated by utilizing the emitted CO$_2$ for synthesizing fuels, thus having a closed sustainable loop of combustion and recycling. The methanol economy presents such a scenario, where CO$_2$ from point-sources in the short term and air-capture in future endeavours is reacted with H$_2$ to create methanol$^{[1-4]}$. Having H$_2$ produced from renewable electricity by electrolysis makes this fuel feedstock sustainable. The bulk chemical of methanol is a resource used both as a combustion fuel or additive to gasoline and more importantly as a feedstock for synthesizing other products such as formaldehyde, dimethyl ether, acetic acid and olefins$^{[5]}$. The commercial production of methanol uses syngas reacted over Cu/ZnO/Al$_2$O$_3$$^{[6–9]}$, where the syngas consisting of a mixture of H$_2$, CO$_2$ and CO is mostly supplied from steam reforming of natural gas or gasification of coal. This methanol catalyst system has been highly optimized through the last century with typical working conditions around 200-300 °C and 50-100 bar pressure, but with the drawback that sintering of Cu nanoparticles reduces their activity over time$^{[10,11]}$. Furthermore CO in the feed-gas is necessary to thermodynamically hinder the production of water from CO$_2$ through the reverse water gas shift reaction (rWGS) which inhibits the methanol synthesis$^{[9,12]}$. The desire to use mainly CO$_2$ as a carbon-source therefor requires new catalysts that are able to suppress the rWGS by higher selectivity. Given the potential of methanol as a sustainable energy carrier on a global scale$^{[13-19]}$ and the need for utilizing delocalized production in more rural and underdeveloped regions, there is a desire to develop novel catalysts that work sufficiently at lower pressure and temperature than the current large methanol plants and with sufficient selectivity and resistance to sintering.

A development from the well-established Cu/ZnO is the use of post-transition metals such as gallium and indium. Even though these materials are much more costly than Cu and Zn, they behave differently to their industrial counter-part making them interesting for research into novel catalysts. One rather unconventional reaction mechanism discovered is the active site formed by producing water, leaving oxygen vacancies in In$_2$O$_3$, which gets remedied by CO$_2$ bonding and formation of methanol since the reaction-pathway for forming CO is not energetically favoured$^{[13,14]}$. Experimental work showed that In$_2$O$_3$ is very selective and stability-wise outperforms Cu/ZnO/Al$_2$O$_3$ when reacting CO$_2$ and H$_2$ in 1:4 at 300 °C and 5 MPA$^{[15,16]}$. Improvement of this catalyst has been achieved through doping of metals e.g. Pd$^{[17–19]}$. Also reported is the use of Ga$_2$O$_3$/Pd by Fujitani et al. which at the time competed well with the Cu/ZnO based catalyst$^{[20]}$. For the renowned Cu/ZnO/Al$_2$O$_3$ Ga$_2$O$_3$ has been used as a structural promoter for dispersing the copper$^{[21]}$. 

Supporting information for this article is given via a link at the end of the document.

[a] T. E. L. Smithhuysen, Prof. I. Chorkendorff, Prof. C. D. Damsgaard
Surfac, Department of Physics
Technical University of Denmark
Fysikvej, Building 311, DK-2800 Lyngby (Denmark)
E-mail: cdda@dtu.dk
[b] Dr. M. R. Nielsen, Prof. C. D. Damsgaard
DTU Nanolab
Technical University of Denmark
Fysikvej, Building 307, DK-2800 Lyngby (Denmark)
[c] Dr. T. Prueßmann, Dr. A. Zimina, Dr. T. L. Sheppard, Prof. J.-D. Grunwaldt
Institute for Chemical Technology and Polymer Chemistry
Karlsruhe Institute of Technology
Engesserstr. 20, D-76131 Karlsruhe (Germany)
[d] Dr. T. L. Sheppard, Prof. J.-D. Grunwaldt
Institute of Catalysis Research and Technology
Karlsruhe Institute of Technology
Hermann-von-Helmholtz Platz 1, 76344 Eggenstein-Leopoldshafen (Germany)
but also actively promoting the reaction. Medina et al. investigated Cu-Ga supported on silica, where it was found that gallium improved the methanol selectivity and the intrinsic activity of Cu. They found using in situ DRIFTS that formate species were adsorbed on GaO2 and suggested that Ga2O3 promoted the formation of methanol by adsorbing carbon-species and using H2 migrating from metallic copper.

Apart from using solid oxides, forming intermetallics of transition metals with gallium or indium as very active catalysts has been achieved with good results in the last decade. Well-known methanation and Fischer-Tropsch catalysts have been adjusted this way towards making methanol. Most notably is the Pd2Ga2 that has been reported as a very active methanol catalyst with an intrinsic activity at least double that of Cu/ZnO/Al2O3. Pd-based intermetallics such as Pd2Ga2 and PdZn have also shown able to perform the syngas-to-dimethyl ether reaction with notable activity and doing so more selectively and stable than Cu/Zn. Pd-In and Ni-In alloys has also been synthesized, where the similar Pd-In proved most active but the In2Pd was much more selective, explained by the fact that the indium is partly oxidized in the In2Pd-alloy. Furthermore Co-Ga3 and Ni-Ga3 catalysts have been discovered based on determination and optimizing of the rate-limiting reaction step based on work done by Grabow et al. on the Cu(111) face. Especially the Ni2Ga has been found to be the most active, but the catalyst struggles through deactivation by coking.

Given the previous success of making active catalysts for methanol synthesis using alloys composed of gallium together with other transition metals, the research presented in this article will evolve around the compositional phase-space of Ni-Fe-Ga. Recent papers showing ternary alloys for hydrogenation of alkynes have inspired the screening of Ni2FeGa2 for methanol synthesis presented in this article, especially the Heusler alloys, which are a frequent intermetallic crystalline phase for ternary transition metal alloys.

In this work a screening consisting of five different Ni2FeGa2/SiO2 has resulted in an active Ni2FeGa2/SiO2 catalyst. Afterwards this catalyst has been optimized in its synthesis procedure and studied using in situ characterisation methods. The final catalytic system is one that selectively produce methanol at 160-200°C and is stable for 100+ hours at 190°C. At high temperatures beyond 200°C it suffers from lower selectivity and activity compared to commercially supplied Cu/ZnO/Al2O3/MgO.

Results and Discussion

Ni-Fe-Ga/SiO2 survey study

**Catalytic performance of the Ni-Fe-Ga/SiO2 catalysts.** In order to find an optimized composition of Ni-Fe-Ga/SiO2, five different catalysts with variable Ni:Fe:Ga concentrations were prepared for the methanol synthesis reaction, all reduced at 800°C for eight hours in H2 directly before running the reaction. The starting point was taken from the Heusler intermetallic of Ni2FeGa expected nominal composition, which has been produced as supported nanoparticles before, and making different catalysts with increasing amount of gallium in them, and so Ni2FeGa1.3 and NiFeGa2 were tested. Additionally the binary alloys of NiFe and FeGa were tested: NiFe since it was desired to try a catalyst in the setup that did not contain gallium even though Ni-Fe alloys have already been reported and FeGa because Fe-Ga alloys have to our knowledge not been published for any catalytic reaction. Testing the catalytic activity of pure iron and nickel were not performed, as they are well known hydrocarbon-catalysts. In Figure 1 the yield of methanol and selectivity are shown recorded at different temperatures.

![Figure 1](image)

**Figure 1.** Top, the methanol yield per mole of Ni, Fe and Ga. Bottom, the methanol selectivity of the tested Ni-Fe-Ga/SiO2. The noted composition is the expected nominal composition. FeGa is neglected from the selectivity because it did not produce a measureable amount of any detected gases. Reaction conditions: 1.2 bar, 100 ml/min of CO2/h in 1-3, GHSV of 8000 h-1, and a GHSV per weight of 130000 Ncm3 h-1 gcat-1. Detected by-products are CO, CH4 and C2H4 and concentrations of these are shown in Figure S2 in the supplementary. Dimethyl ether was not measured beyond the detection limit. Uncertainties are estimated by propagation of error.

Regarding the activity of the tested catalyst, the stoichiometric Heusler Ni3FeGa reached the highest methanol rate, though compared to Cu/ZnO/Al2O3/MgO under similar conditions in Figure 3, it have only one third of the activity. Increasing the content of gallium reduced the rate of methanol formation but increased the selectivity to methanol. With the lowest methanol rates and selectivities are NiFe and FeGa: NiFe because it produced much more CO and methane as shown in Figure S2 of the supplementary; FeGa surprisingly did not produce any measurable quantity of gaseous products in the tested temperature-range. Especially because as mentioned earlier gallium alloyed with Co, Ni, Cu and Pd has been reported catalytically active, thus the state of FeGa tested in this work must be vastly different.

Besides the different activities, all the catalyst behaved in the same manner, showing decreased methanol formation rate at elevated temperatures, which is due to the increased CO production inhibiting the methanol equilibrium through the production of water by WGS. All catalysts showed optimum methanol yield at temperatures around 210°C though this optimum is readily controlled by the gas velocity.
Crystalline phase and chemical composition of Ni-Fe-Ga catalysts. To support the activity experiments, characterization of the catalysts was done ex situ to the activity experiments using XRD, TEM and SEM-EDX. Table 1 shows the macroscopic composition of Ni, Fe and Ga normalised to a Heusler stoichiometry (sum of four). Here it is apparent that within a standard deviation, the expected nominal and measured composition prior and after catalytic experiments are the same, except for the FeGa where prior and post composition differs little from a single standard deviation. Therefore the different catalysts will be referred to with their nominal composition.

Presented in Figure 2 are XRD-patterns of all the respective alloys alongside TEM images showing the Ni$_2$FeGa nanoparticles supported on silica. Supporting the XRD patterns are reference lines for face centred and body (3.6 Å) centred cubic crystal (2.9 Å)-structures showing that in all cases these two structures explain the diffraction peaks, except for FeGa. FeGa has additional peaks that fit with a diamond crystal-structure. The transition between the fcc and bcc structures go from NiFe with a very clear fcc structure to a bcc when adding more gallium to the alloy. In the case of the most active alloy Ni$_2$FeGa, clear trends of both fcc and bcc are present, showing both individual peaks and as a shoulder on the most intense peak at a 20-angle of 44°. Taken that Ni, Fe and Ga are close in the periodic table and the scattering cross-section of X-rays is proportional to the second power of the atomic charge, intermetallic structures are hard to distinguished from random alloyed structures, but the size of the crystalline unit-cell corresponds very well to a Heusler crystal in the bcc case and a tetragonal Heusler or γ-Heusler in the fcc case. As no long-range order has been observed, the alloyed crystal structures will be noted as bcc and fcc as well.

The acquired HR-TEM images shown in Figure 2, top right, and Figure 2s in the supplementary information show that the crystalline phase of the nanoparticles to be the fcc structure, but the difference between (111)-planes of fcc and (110)-planes of bcc is less than 0.02 Å making them indistinguishable. Alloyed Ni$_2$FeGa nanoparticles are not expected to be phase-pure since Ni$_2$FeGa is known for being difficult to synthesize in a pure single crystal phase[2]. Figure S3.0 of the supplementary shows two HR-TEM images, where two different crystal phases are visible within the sample nanoparticle. Even in the case where an intermetallic long-range order is achieved of either Heusler or tetragonal Heusler, Ni$_2$FeGa has been shown to be able to undergo the martensitic transformation similarly that of iron going continuously from a bcc to an fcc structure, both for alloyed ribbons and for large single crystals[47–50]. Therefore it is likely that Ni-Fe-Ga alloyed nanoparticles individually pick between fcc and bcc phases dependent on small fluctuations in the local atomic environment or the chemical composition of the three components. The compositions were found to fluctuate from nanoparticle to nanoparticle, as ex situ STEM-EDX and STEM-EELS of Ni$_2$FeGa shows, Table S2 in the supplementary. This observation also substantiates the claim that ternary-alloyed nanoparticles have been made.

BF-TEM images like the one shown in Figure 2, bottom right, were acquired for all the tested catalysts, exemplified in Figure S4 in the supplementary information. Size distributions based on BF-TEM in Table 1 show a trend, where more gallium-rich alloys produce smaller nanoparticles. FeGa and NiFe have on average 2.6 nm larger nanoparticles than the gallium-containing ternary alloys. For the ternary alloys the resulting nanoparticles are smaller, where the largest particles from Ni$_2$FeGa are also the ones with the highest methanol yield. Thus the difference in activity towards making methanol is not explained by difference in surface areas.

In part conclusion, addition of gallium has changed the selectivity of Ni-Fe catalysts from methane towards methanol. Furthermore the survey has shown that there is an optimum of gallium content for improving the activity, but this can be done only at the expense of selectivity.

Optimization of Ni$_2$FeGa/SiO$_2$

Catalytic performance of the Ni-Fe-Ga/SiO$_2$ catalysts. Following the screening-study, the most active catalyst i.e. Ni$_2$FeGa/SiO$_2$ was optimized further in terms of reduction temperature. 800 °C in high concentrations of H$_2$ for eight hours was initially chosen based on literature[38,39,42]. Therefore
samples of Ni$_2$FeGa/SiO$_2$ were prepared by 4 hours of reduction at 300 °C, 400 °C, 500 °C, 550 °C, 600 °C and 700 °C respectively, after which they were all tested for their catalytic activity. Figure 3 shows the outcome in terms of methanol yield and selectivity both in terms of reduction temperature and compared to our prepared sample of the commercially available Cu/ZnO/Al$_2$O$_3$/MgO.

![Figure 3. Top, the yield of methanol per mole of active metal (Ni, Fe and Ga) of Ni$_2$FeGa/SiO$_2$ versus the reduction temperature used in preparation of the catalyst. Bottom, the methanol selectivity of Ni$_2$FeGa/SiO$_2$ versus the reduction temperature. All points on the plot show individual test of Ni$_2$FeGa/SiO$_2$ all reduced in 90% H$_2$/Ar for 4 hours prior to the activity experiment, except for the 800°C-sample that was reduced for 8 hours. Reaction conditions: 208°C, 1.2 bar, 100 ml/min of CO$_2$/H$_2$ in 1:3, GHSV of 8000 h$^{-1}$ and a GHSV per weight of 130000 Ncm$^{-3}$ h$^{-1}$ g$_{FeGa}^{-1}$ or Ncm$^{-3}$ h$^{-1}$ g$_{Cu}^{-1}$. Catalysts were all tested at different temperatures, which is shown in Figure S6 in the supplementary information.](image)

A clear optimum in catalytic performance is found when the Ni$_2$FeGa/SiO$_2$ has been reduced at 550 °C for 4 hours, both in terms of methanol yield and selectivity, where both values are increased two-fold compared to the sample reduced at 800°C for 8 hours. As Figure 3 Top clearly shows there is an increase and decrease in both methanol yield and selectivity around the reduction temperature of 550 °C, showing that two different formation processes must take place at low and high reduction temperatures. Ni$_2$FeGa reduced at 550 °C performs similarly at low temperature as the Cu/ZnO/Al$_2$O$_3$/MgO but is outperformed at higher temperatures as Figure 3 bottom shows. In literature the most similar catalyst would be Ni$_2$Ga$_2$/SiO$_2$ reported by Studt et al., which is similar in activity compared to Cu/ZnO[33] and thus also more active than Ni$_2$FeGa. The obtained activity of Ni$_2$FeGa in this work is achieved with lower gallium content and with a 150 °C decrease in reduction temperature compared to Ni$_2$Ga$_2$/SiO$_2$ as it was reported[34].

Especially at reaction temperatures above 200 °C, the Ni$_2$FeGa performance falls short of the Cu/ZnO/Al$_2$O$_3$/MgO, which is due to the lower activity of Ni$_2$FeGa and poisoning through coking at higher temperatures. On repetition of the catalytic test, the Ni$_2$FeGa had lost almost half its activity after being heated to 250 °C in reaction conditions. It could easily be regenerated through reduction in H$_2$ producing methane and methanol in the process. This is shown in Figure S7-8 in the supplementary. Long-term stability test of Ni$_2$FeGa/SiO$_2$, in Figure S8 right, showed an initial decrease in activity over a course of hours before keeping a stable methanol yield and selectivity for 100 hours. Upon reactivation in H$_2$, the initial activity and selectivity are obtained.

Based on size-distributions from an ex situ TEM analysis of the Ni$_2$FeGa/SiO$_2$ catalysts reduced at ≥550 °C, surface activity has been estimated and found not to be significantly different for these samples, which means that loss in activity due to a higher reduction temperature is mainly due to decrease in surface-area through sintering. This is shown in Figure S10 of the supplementary in terms of size distributions and surface activity versus reduction temperature plots.

**In situ investigation into the reduction and thereby the formation of Ni$_2$FeGa/SiO$_2**.

To understand the properties achieved through reducing at different temperatures and why 550 °C is an optimum, several in situ methods were utilized during the reduction of metal-nitrides into the Ni$_2$FeGa/SiO$_2$, which are E-TEM, XRD and XANES/EXAFS.

**Environmental Transmission Electron Microscopy.** Visualization of a fresh non-reduced sample of Ni$_2$FeGa showed that nanoparticles were very hard to detect until heating the sample to 300 °C. The area illuminated during heating is shown in Figure S11 of supplementary, showing that nanoparticles are not visible at 200 °C. Figure 4 presents HR-TEM images taken at 300 °C and 550 °C alongside size-distributions made for these temperatures. The atomic planes found with HR-TEM show both metallic nanoparticles with close-packed planes of ~2.1 Å agreeing with the ex situ XRD, and particles with larger interplanar distances of 2.4 Å and 2-9 Å which could be oxides. Here it has been found that the nanoparticles grew in size from an average of 3.4 nm to 3.8 nm when heating from 300 °C to 500 °C. During the microscopy, STEM-EDX was performed on individual nanoparticles by parking the beam and acquiring an EDX-spectrum. The quantifications of all the spectra are gathered in Table S3 in the supplementary.

![Figure 4. Left, in situ HR-TEM images, at 300°C a large oxide particle with interatomic spacing of 2.4 Å and 2.9 Å, and two small metallic nanoparticles showing ~2.1 Å interatomic spacing. At 500°C the quantity of the latter having fringes of 2.1 Å has increased. Right, size-distribution based on in situ TEM images, showing a small increase in the sizes of the nanoparticles at higher temperature.](image)
Due to time constraints only 9 individual spectra were acquired which is not nearly statistically significant. Nonetheless comparing STEM-EDX with SEM-EDX of the whole sample stated in Table S4 in the supplementary, show that on average the concentration of iron and gallium is lower than the macroscopic measurement. Thus, if the nanoparticles are representative, the different Ni-species are reduced more than the corresponding Fe- and Ga-species. This corresponds very well to the fact that oxides such as FeO and Ga₂O₃ have a higher formation enthalpy and are harder to reduce compared to NiO[51,52]. This also means that an enlargement of the nanoparticles from 300 °C to 500 °C is not sintering, as this would show on the yield per mass of methanol, but instead the reduction of new species that alloy in the nanoparticles.

**In Situ X-ray Diffraction.** Reducing the metal-nitrides into Ni₃FeGa/SiO₂ in H₂ while performing XRD showed large changes of the crystalline structure together with production of various gases measured by QMS, both results shown in Figure 5 and 6. From the XRD Fig. 5, broad peaks appear at 100-300 °C producing 2θ-peaks at ~35° and ~60°, which can very well be Fe₂O₃ (ICSD cc.: 15840), Fe₃O₄ (ICSD cc.: 26410) or Ga₂O₃ (ICSD cc.: 34243). Metal nitrates decomposing into solid oxides agrees well with the QMS Fig. 6, where at 100 °C multiple species are produced being H₂O, NO, and CO₂, and at 200 °C N₂ is produced. H₂O rises again at 250°C, which correlates with a 2θ-peak at 43° appearing in the XRD pattern. This corresponds very well to an fcc phase of Ni (ICSD cc.: 43397) or Ni₃Fe (ICSD cc.: 5116, 103555, 103559), especially because the peak intensifies as the temperature rises together with corresponding fcc-peaks appearing at 350°C. In principle the 2θ-peak at 43° could also be FeO (ICSD cc.: 31081) or NiO (ICSD cc.: 9866) as these would be intermediates before forming metallic nanoparticles but if this is the case, they are very ephemeral. At 550 °C H₂O rises again, very well corresponding to Ga₂O₃ finally being reduced and alloying into the metallic nanoparticles, which is showing as two new 2θ-peaks appearing at 75° and 51° at very low intensity at 650°C and 750°C. 2θ-peaks at 44°, 51° and 75° resembles a bcc phase corresponding to the Heusler crystal structure of Ni₃FeGa (ICSD cc.: 157384), though it might not be intermetallic but random in its atomic positions. In conclusion this means that from lower to higher temperatures, the nanoparticles appear to transition from pure Ni into Ni-Fe and finally in the ternary alloyed Ni-Fe-Ga, when the temperature is high enough that Fe and Ga can be reduced. This agrees with the in situ ETEM where it has been concluded that small nanoparticles at low temperatures are containing mostly nickel.

**In Situ X-ray Absorption Spectroscopy.** The real-space Fourier-transform of the extended fine structure of all the measured edges are shown in Fig. 7. The results show for all edges that when heating in H₂, amplitudes from back-scattering on the nearest neighbour elongate from ~1.8 Å to 2.2 Å. Furthermore at well above 200 °C, this structure is still apparent. Since the nitrate-salts will be decomposed at such temperatures as the mass spectroscopy from the in situ XRD shows in Figure 5, this must be scattering from an oxygen neighbour showing that the metals are only partially reduced at lower temperatures. Comparing the different edges it is also obvious that nickel is reduced much more easily than iron and drastically more than gallium, which agrees with the analysis from the in situ XRD and ETEM. Linear combination fitting of the XANES using the oxides and the metal at the corresponding edge gave additional insight into the reduction behavior (Figure S16-19 in the supplementary information). All the edges show intermediate species of oxides when heating from low to high temperatures in agreement with EXAFS and XRD as well.

**In Situ XRD**

![In Situ XRD](image)

**Figure 5.** In situ XRD of the formation of Ni₃FeGa/SiO₂ a fresh non-reduced sample, while heating the sample in 90% H₂/He. Lines denote reference-patterns of a face centred cubic lattice and a body centred cubic lattice, with a cubic unit-cell length of 3.6 Å and 2.9 Å. X-ray source was a Cu-Kα anode with wavelength 1.5418 Å.

**Figure 6.** Fourier-filtered Quadrupole Mass-spectroscopy of the outlet gas during in situ XRD. Parentheses denote the detected mass. All detected masses and unfiltered data are shown in Figures S12-14 in the supplementary.

**Figure 7.** In situ real-space represented K²-weighted EXAFS of the formation of Ni₃FeGa/SiO₂ from a fresh non-reduced sample. Samples were heated at the denoted temperature in 5% H₂/He, and subsequently cooled to 50°C for a proper acquisition of the absorption spectrum. Corresponding XANES are shown in Figure S16 in the supplementary. The dotted lines show fits to data acquired after heating at the highest temperature with parameters given in Table 2. Two separate samples were experimented on, firstly measuring the Ni and Fe K-edges, and subsequently measuring the Ga K-edge.
though no further substantial analysis went into illuminating this was into producing methanol synthesised, Ni/Fe/Ga of an oxygen spectrum. Furthermore the direct back-scattering paths from Ni, Fe and Ga species could not be distinguished, as the scattering amplitudes were so correlated that only the sum could be determined by the data. The coordination number has been defined to this value, as the determined value of the amplitude S<sub>0</sub> from the reference foil is too low to keep fitting of the coordination number within physical limits. GaO<sub>2</sub> has two non-equivalent positioned gallium-atoms within its unit cell, meaning that three almost identical scattering paths happen within the first 1.91 Å. These paths have been collectively written in the table as a single O-atom. Furthermore, the coordination of the Ni/Fe/Ga crystal structure was used for fitting the Ni and Fe K-edges, while both γ-Ni<sub>2</sub>FeGa and GaO<sub>2</sub> was used for the Ga K-edge.

<table>
<thead>
<tr>
<th>Edge</th>
<th>Neighbour&lt;sup&gt;+&lt;/sup&gt;</th>
<th>N&lt;sub&gt;i&lt;/sub&gt;</th>
<th>R&lt;sup&gt;0&lt;/sup&gt; (Å)</th>
<th>σ&lt;sup&gt;0&lt;/sup&gt; (Å)</th>
<th>Residual factor</th>
<th>Fitting range (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni K</td>
<td>Ni/Fe/Ga</td>
<td>11.0 ±1.0</td>
<td>2.52 ±0.01</td>
<td>0.008 ±0.001</td>
<td>0.013</td>
<td>1.0 to 4.1</td>
</tr>
<tr>
<td></td>
<td>Ni</td>
<td>4.4 ±1.3</td>
<td>3.56 ±0.01</td>
<td>0.012 ±0.001</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ni/Fe/Ga</td>
<td>15 ±4</td>
<td>4.36 ±0.01</td>
<td>0.014 ±0.001</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe K</td>
<td>Ni/Ga</td>
<td>12.0&lt;sup&gt;±&lt;/sup&gt; ±1.6</td>
<td>2.51 ±0.01</td>
<td>0.010 ±0.001</td>
<td>0.026</td>
<td>1.0 to 4.1</td>
</tr>
<tr>
<td></td>
<td>Fe</td>
<td>4 ±2</td>
<td>3.55 ±0.01</td>
<td>0.014 ±0.001</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ni/Fe</td>
<td>15 ±6</td>
<td>4.35 ±0.01</td>
<td>0.018 ±0.002</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ga K</td>
<td>O&lt;sup&gt;2-&lt;/sup&gt;</td>
<td>5.7 ±0.3</td>
<td>1.81&lt;sup&gt;±&lt;/sup&gt; to 1.91&lt;sup&gt;±&lt;/sup&gt; ±0.02</td>
<td>0.006 ±0.004</td>
<td>0.010</td>
<td>1.1 to 4.0</td>
</tr>
<tr>
<td></td>
<td>Ni/Fe</td>
<td>6.4 ±0.4</td>
<td>2.51 ±0.01</td>
<td>0.011 ±0.001</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Fe/Ga</td>
<td>2.2 ±0.5</td>
<td>3.55 ±0.01</td>
<td>0.016 ±0.001</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ni/Ga</td>
<td>8.2 ±1.3</td>
<td>4.35 ±0.01</td>
<td>0.019 ±0.002</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

[a] Change in Scattering-length and Debye-Waller factor have been fitted for each crystal structure, and not for each individual scattering-path. [b] Ni, Fe and Ga species could not be distinguished, as the scattering amplitudes were so correlated that only the sum could be determined by the data. The coordination number has been defined to this value, as the determined value of the amplitude S<sub>0</sub> from the reference foil is too low to keep fitting of the coordination number within physical limits. GaO<sub>2</sub> has two non-equivalent positioned gallium-atoms within its unit cell, meaning that three almost identical scattering paths happen within the first 1.91 Å. These paths have been collectively written in the table as a single O-atom. Furthermore, the coordination of the Ni/Fe/Ga crystal structure was used for fitting the Ni and Fe K-edges, while both γ-Ni<sub>2</sub>FeGa and GaO<sub>2</sub> was used for the Ga K-edge.

The best catalyst in this study was found to be Ni<sub>2</sub>FeGa/SiO<sub>2</sub>. After optimization of the catalyst preparation, the most active and selective catalyst was found by reducing in H<sub>2</sub> at 550°C for four hours. This final catalyst was compared to a commercial copper-based methanol synthesis catalyst, achieving similar activity at temperatures below 200 °C, but higher temperatures caused the Ni<sub>2</sub>FeGa to suffer from lower selectivity and coking.

Comprehensive in situ characterisation of the Ni<sub>2</sub>FeGa using XRD, TEM and XAS showed how it can alloy from Ni-, Fe- and Ga-nitrate salts. The optimized reduction temperature of 550 °C is exactly the heat-limit at which the Ni<sub>2</sub>FeGa is forming in fully ternary metallic nanoparticles, but also cold enough that small nanoparticles are produced increasing the surface area.

Ni<sub>2</sub>FeGa/SiO<sub>2</sub> cannot currently out-perform other state-of-the-art catalysts in the field, however, this work shows how the approach of using multiple species with different reduction potential can offer an advantage: producing small alloyed catalytically active nanoparticles.

**Experimental Section**

**Synthesis**

The synthesis of SiO<sub>2</sub> supported Ni<sub>2</sub>FeGa nanoparticles was performed using incipient wetness impregnation and subsequent reduction in H<sub>2</sub> at elevated temperatures. Nickel(II)nitrate hexahydrate (10816, Alfa Aesar), iron(III)nitrate nonahydrate (529303, Sigma-Aldrich) and gallium(III)nitrate hydrate (11150, Alfa Aesar) were diluted in millipore water and impregnated in ground high surface area silica powder (44740, Alfa Aesar) resulting in 16.7 wt% metal loading on SiO<sub>2</sub>. Nominal loadings and EDX analysis of composition can be found in Table 1 and Table S1, S2 in the supplementary info. The powder had a grain-size of 105-210 µm. Impregnated silica was subsequently dried for 2 hours at 80 °C in air after which they were loaded in quartz glass-tube...
reactors to allow a plug-flow and heated using a tube furnace. Here they were reduced in 1.2 bar 90% H₂ in Ar at 800 °C for eight hours before being tested in the same reactor for their catalytic performance. Pellets of CuO(63.5%)/ZnO(24.7%)/Al₂O₃(10.1%)/MgO(1.3%) (45776, Alfa Aesar) were purchased and ground to a grain-size of 105-210 µm and diluted with SiO₂ (the same material used as the support of Ni₅Fe₃Ga₅). The powder was loaded in a quartz glass-tube reactor and reduced in 1.2 bar 10% H₂ in Ar at 220 °C for 3 hours, then subsequently tested for its catalytic activity. The preparation of the commercial catalyst ensures that CuO is reduced to Cu. The choice of preparation is based on a TPR, shown in Figure S1 in the supplementary. Dilution of the commercial catalyst in SiO₂ was done to achieve equal weight of Cu and Ni₅Fe₃Ga₅ while also having equal geometric dimensions of the reactor-bed. ZnO and MgO are here considered as being support-material of the commercial catalyst.

Catalytic testing

Directly after reducing the catalysts in the plug-flow reactor, the reactor was cooled down to 130 °C and the gas-flow changed to 25% CO₂, 75% H₂ and traces of Ar at 1.2 bar, with a GHSV of 8000 h⁻¹ and a GHSV per weight of 130000 Ncm⁻³ h⁻¹ for Cu₄Ga₃O₅ or Ncm⁻³ h⁻¹ for CuO. Exact weights of loaded catalyst are written in Table S1 in the supplementary. The reactor-temperature was changed step-wise up and down twice between 145 °C and 250 °C in 15 C/step and with 1.5 hours steady-state per step. Gas samples were collected approximately every 45 mins at the reactor-exhaust with a gas chromatograph (Agilent 7890a) mounted with a TCD and FID using separate columns and lines: 80/100 HATESEQ packed column for moisture removal, 19095P-Q40 capillary column and 19095P-M6 molecular sieve column on the TCD-line; 19091J-413 capillary column on the FID line. Any gas sample taken close to a temperature-change was discarded.

Characterisation

Transmission electron microscopy (TEM) and spectroscopy. After catalytic tests, samples were loaded on a 300-mesh lacy carbon Au TEM-grid (AGS166A3H, Agar Scientific). Bright-field imaging for nanoparticle size-distributions was performed in ultra-high vacuum on a Tecnai T20 G² (FEI) with a LaB₆-thermic filament operated at 200 keV. Size-distributions (Figure S9) were measured by drawing the outline of each observed nanoparticle, measuring the area and calculating a corresponding circular diameter. High Resolution TEM (HR-TEM) and STEM including energy dispersive X-ray spectroscopy (EDX) and electron energy loss spectroscopy (EELS) were performed in ultra-high vacuum on a Titan E-Cell 80-3000ST TEM (FEI) with a FEG operated at 300 keV on two samples of Ni₅Fe₃Ga₅/SiO₂ after reduction and catalytic testing: one reduced at 500 °C and one at 800 °C (Figure S3).

Powder X-ray diffraction (XRD). Samples having undergone catalytic testing were pressed to pellets in steel-casings designed for powder XRD. The XRD was performed on the samples in an Empyrean (Malvern Panalytical) with a CuKα-anode. The diffraction beam was filtered through a monochromator and the sample was spun with 3.75 rotations/min.

Scanning electron microscopy (SEM) and EDX. Powder samples both before and after synthesis and test in the plug-flow reactor were loaded on Aluminium stubs with double carbon-tape. SEM-EDX was performed using a Quanta FEG 200 ESEM (FEI) operated at 20 keV and a 0.1 bar vapour pressure. EDX data was collected using an 80 mm² X-Max silicon drift detector (Oxford instruments) with 124 eV energy-resolution. The procedure was to scan the beam well within individual catalytic grains for between 30-60 seconds to gather a converged EDX-spectrum. A minimum of eight spectra were gathered for each individual sample.

Environmental transmission electron microscopy and spectroscopy. Impregnated sample of stoichiometry Ni₅Fe₃Ga₅ was ground and diluted in 1.2 propanol after which it was immediately drop-casted on a Nanochip XT through-hole chip (DENSolutions), in minimal amount to allow for TEM-transparency. After drying in air the chip was loaded on a DENSolutions Wildfire heating holder and loaded into a Titan E-Cell 80-3000ST TEM (FEI) with a FEG operated at 300 keV. A continuous flow of H₂ at 1.2 mbar was set and the sample was briefly viewed in TEM-mode and low magnification before heating the sample. The sample was heated chronologically to 200 °C, 300 °C and 500 °C while during BF-TEM. At lowest magnification and a spread beam the sample was briefly investigated in order to find proper spots where the sample was sufficiently transparent. A spot was chosen for imaging when heating and cooling, and all other imaging was conducted on un-exposed areas in order to minimise beam damage. HR-TEM and STEM-EDX were performed interchangeably after heating to 300 °C and 500 °C.

In situ X-ray diffraction and quadrupole mass spectrometry (QMS). Impregnated sample of stoichiometry Ni₅Fe₃Ga₅ was loaded on a ceramic holder and mounted into a furnace with X-ray transparent beryllium windows (XRK 900, Antoon Paar) situated within an Xpert Pro diffractometer (Malvern Panalytical) with a CuKα-anode. The diffraction beam was filtered through a monochromator. A continuous flow of H₂ at 1 bar was set and with a gas velocity matching the synthesis and catalytic tests performed in the plug-flow reactor. The sample was heated to 750 °C in steps of 50 °C and with three diffraction-angle scans at each temperature over 1.7 hours. The gas-exhaust was monitored using QMS supplied by Pfeiffer. In order to filter mass-signals from heating and desorption of surface-condensed water, a high-frequency bandwidth-filter was applied to the QMS data. All raw data, filtering and resulting reduced data is available in Figure S13-15 in the supplementary. The Inorganic Crystal Structure Database (ICSD)[53] has been used for recognizing different crystal structures and ICSD collection codes are noted in parentheses when discussed in the text.

In situ X-ray absorption spectroscopy (XAS). Impregnated sample of stoichiometry Ni₅Fe₃Ga₅ was loaded into a 1.5 mm(θ) capillary with a bed length of 4 mm and a gas-flow of 5% H₂ in He with pressure equilibrated with the atmospheric conditions. XAS experiments were performed at the CAT-ACT beamline at the synchrotron light facility at Karlsruhe Institute of Technology[54]. Heating was performed with a gas-blower and Eurotherm heat regulator and energy was calibrated from a reference metal foil chosen dependant on the measured edge. Spectra for an analysis of the EXAFS were all acquired at 50 °C after treating the sample at higher temperatures (see below), and quick XANES spectra were acquired while heating the sample. The procedure of the experiment was to heat the sample for a specific duration of time before cooling down to 50 °C and acquiring a spectrum for EXAFS, then subsequently heating the sample again to a higher temperature. Two individual experiments were performed at different times with a modestly varying setup: one for acquiring the Ni and Fe K-edges with a gas-flow of 3 ml/min, and one for acquiring the Ga K-edge with a gas-flow of 50 ml/min. For the Ni and Fe K-edges the sample was heated to 248 °C for 50 mins, 375 °C for 30 mins and 581 °C for 10 mins, all with a heating ramp of 40 °C/min at which XANES of the Ni and Fe K-edges were acquired. For the Ga K-edge the sample was heated to 222 °C for 50 mins, 339 °C for 30 mins and 498 °C for 10 mins, all with a heating ramp of 10 °C/min at which XANES of the Ga K-edge was acquired. This procedure was devised during the experiment based on the time at which the XANES of the Ni K-edge did not change noticeably.

Absorption was in all experiments measured in transmission mode with a reference foil: A Fe-foil for the Fe K-edge, a Ni-foil for the Ni K-edge and a W-foil for the Ga K-edge. Data was calibrated and normalised using Athena[55] and subsequently the EXAFS acquired after heating at the highest temperature were fitted using Artemis[56]. Linear combination fitting has been done and is available in Figure S16-19 in the supplementary.

Acknowledgements

The A.P. Møller and Chastine McKinney Møller Foundation is gratefully acknowledged for the contribution towards the establishment of the Center for Electron Nanoscopy in the Technical University of Denmark. We would like to thank the Institute for Beam Physics and Technology (IBPT) for the operation of the storage ring, the Karlsruhe Research Accelerator (KARA). We acknowledge the

This article is protected by copyright. All rights reserved.
This article is protected by copyright. All rights reserved.