

Technical University of Denmark



## Origin of low temperature deactivation of Ni<sub>5</sub>Ga<sub>3</sub> nanoparticles as catalyst for methanol synthesis

Gardini, Diego; Sharafutdinov, Irek; Damsgaard, Christian Danvad; Dahl, Søren; Wagner, Jakob Birkedal

*Publication date:*  
2012

[Link back to DTU Orbit](#)

*Citation (APA):*

Gardini, D., Sharafutdinov, I., Damsgaard, C. D., Dahl, S., & Wagner, J. B. (2012). Origin of low temperature deactivation of Ni<sub>5</sub>Ga<sub>3</sub> nanoparticles as catalyst for methanol synthesis. Abstract from 15th Nordic Symposium on Catalysis, Mariehamn, Åland Islands.

## DTU Library

Technical Information Center of Denmark

---

### 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.

# Origin of low temperature deactivation of Ni<sub>5</sub>Ga<sub>3</sub> nanoparticles as catalyst for methanol synthesis

D. Gardini<sup>1,2\*</sup>, I. Sharafutdinov<sup>2</sup>, C.D. Damsgaard<sup>1</sup>, S. Dahl<sup>2</sup> and J.B. Wagner<sup>1</sup>

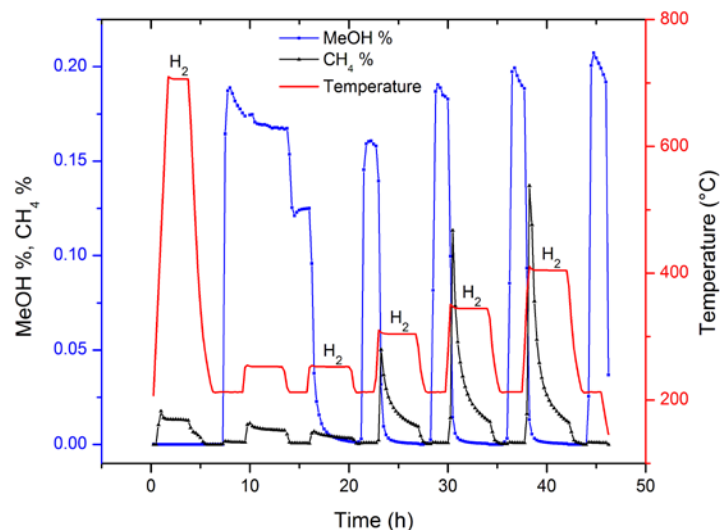
1 - Center for Electron Nanoscopy, Technical University of Denmark, DK-2800 Lyngby, Denmark

2 - Department of Physics, Technical University of Denmark, DK-2800 Lyngby, Denmark

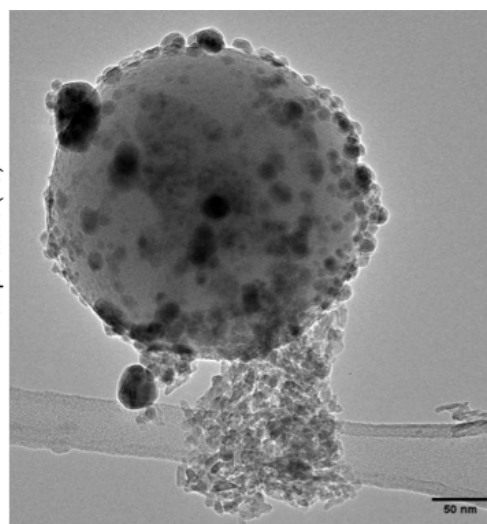
\* E-mail: s101282@student.dtu.dk

In an effort to find alternative energy sources capable to compete with fossil fuels, methanol synthesis could represent a realistic solution to store “green” hydrogen produced from electrolysis or photo-induced water splitting. Recently, density functional theory (DFT) calculations [1] proposed Ni-Ga alloys as active catalysts for methanol production from syngas mixtures and Ni-Ga nanoparticles supported on highly porous silica have been prepared using an incipient wetness impregnation technique from a solution of nickel and gallium nitrates [2]. Tests conducted in a fixed-bed reactor showed that the highest methanol yield is obtained with a Ni<sub>5</sub>Ga<sub>3</sub> alloy exposed to a 25% CO<sub>2</sub> – 75% H<sub>2</sub> reaction mixture at 210 °C [2]. Under these experimental conditions, the catalyst is found to lose 35% of its activity after 20 hours of continuous testing at both 1 and 5 Bars. Although *in situ* XRD and EXAFS studies [3] confirm dealloying as responsible for high temperature (T > 300 °C) deactivation, this does not explain the activity loss in the low temperature regime (T < 300 °C).

This work presents an extensive study on the low temperature (T = 200, 210, 250 °C) deactivation of silica supported Ni<sub>5</sub>Ga<sub>3</sub> nanoparticles as catalyst for methanol production. Synthesis, followed by deactivation and a series of regeneration steps at increasing temperature in pure H<sub>2</sub> has been carried out in a fixed-bed reactor connected to a gas chromatography system. In each regeneration step, CH<sub>4</sub> is generated and the activity of the catalyst is subsequently increased, suggesting the presence of carbon containing species blocking the active sites of the alloy nanoparticles (Figure 1). Carbon deposition has furthermore been investigated by temperature programmed oxidation (TPO) of a deactivated catalyst in a fixed-bed reactor connected to a mass spectrometer. CO<sub>2</sub> and H<sub>2</sub>O evolution at T > 200 °C confirms the presence of carbon containing species on the catalyst. Finally, an electron microscopy study aiming at direct carbon probing has been performed, requiring the synthesis of a new support consisting of 200 nm Stöber silica spheres [4]. Unlike porous silica, on this new support Ni<sub>5</sub>Ga<sub>3</sub> nanoparticles becomes directly exposed to the electron beam (Figure 2) allowing us to obtain high resolution TEM images and perform more accurate electron energy loss spectroscopy (EELS) measurements.



**Figure 1.** Methanol and methane evolution during a regeneration experiment of Ni<sub>5</sub>Ga<sub>3</sub> catalyst.



**Figure 2** TEM image of Ni<sub>5</sub>Ga<sub>3</sub> nanoparticles supported on a 200 nm silica sphere.

## References:

- [1] F. Studt et al., SLAC, Stanford University (to be published).
- [2] I. Sharafutdinov et al., Technical University of Denmark (to be published).
- [3] I. Sharafutdinov et al., Private communication, Technical University of Denmark
- [4] R. Lindberg, J. Sjöblom, G. Sundholm, Colloids Surfaces A 99 (1995) 79-88