ETEM study of deactivation of NiGa nanoparticles as catalyst for methanol synthesis

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NiGa catalysts prepared by incipient wetness impregnation on a high surface area silica support, using a suspension of nickel and gallium nitrates have shown very promising results, revealing the highest methanol yield from Ni_5Ga_3 in a gas mixture of 75% H_2 and 25% CO_2 at 210°C [1,2]. Accelerated aging experiments have been performed at temperatures between 210°C and 400°C. At temperatures 210°C<T<250°C a significant deactivation is observed. The catalyst can be regenerated by a heat treatment at 300°C in H_2. At temperature 300°C<T<400°C the catalyst is deactivated further, and a phase change from Ni_5Ga_3 to Ni_3Ga occurs. In this regime the catalyst activity can be regenerated in H_2 at 700°C [3]. The lower temperature deactivation cannot be assigned to this phase change.

This work presents detailed Environmental Transmission Electron Microscope (ETEM) investigations of the temperature dependent deactivation effects of Ni_5Ga_3 nanoparticles as a catalyst for methanol synthesis. ETEM samples were prepared by dissolving $Ni(NO_3)_2$ and $Ga(NO_3)_3$ in a Ni:Ga ratio of 5:3 in millipore water and subsequently dispersed on TEM sample grids. The sample grid was mounted in a TEM heating holder and inserted in a FEI Titan ETEM with imaging C_s corrector as well as facilities for *in situ* gas reactions operated at 300 kV [4]. The Ni_5Ga_3 synthesis was performed *in situ* at 660°C in a H_2 flow of 2 Nml/min at a pressure of 130 Pa. The deactivation experiments were performed *in situ* at temperatures between 200°C and 450°C in a 75% H_2 and 25% CO_2 laminar flow at a pressure between 100 Pa and 500 Pa. Data was acquired, subsequently, by obtaining bright field TEM images, diffraction patterns (DP), High Resolution TEM (HRTEM) images, and Electron Energy Loss Spectroscopy (EELS) data.

Figure 1 illustrates morphology changes of a single NiGa particle during reduction and activation experiments. a) shows a passivated particle at RT in vacuum, b) shows the reduced particle in H_2 at 350°C, and c) shows the particle in 75% H_2 and 25% CO_2 at 200°C. The reduced particle b) shows a more facetted morphology compared with both the passivated particle a) and the particle exposed to CO_2 c). Both a) and b) show a crystalline particle, however lattice fringes in c) might be hampered by electron scattering by the "heavier" CO_2 molecule. EELS spectrum of the same particle reveals Ni and Ga ionization edges.

The ETEM aging experiments have been supported by complementary *in situ* X-Ray Diffraction (XRD) and activity measurements on deactivation of Ni_5Ga_3 catalyst on a silica support prepared by wet impregnation [2]. Although the *in situ* XRD was performed at significantly higher H_2 flow (40 Nml/min) and pressure (100 kPa) the complimentary data correlates with the main temperature dependence of phase and structure.

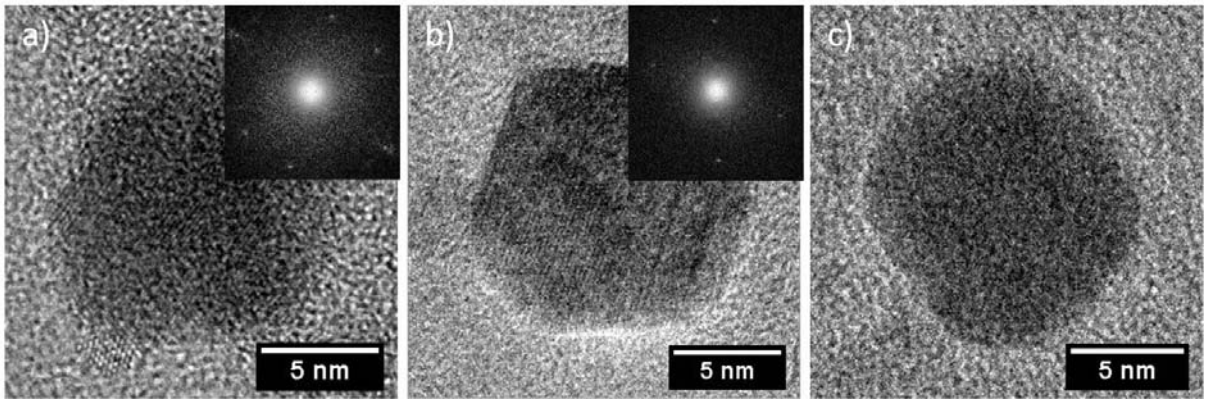

Figure 1. HRTEM and FFT of a) passivated NiGa particle at RT in vacuum, b) the reduced NiGa particle in H_2 at 350°C, and c) the NiGa particle in 75% H_2 and 25% CO_2 at 200°C.

[1] F. Studt et al., SLAC, Stanford University (to be published).
[2] I. Sharafutdinov et al., Technical University of Denmark (to be published).
[3] D. Gardini et al.: Student project, Technical University of Denmark.
[4] T.W. Hansen et al., Materials Science and Technology 11(2010), p.1338.