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In situ microscopy of formation of nickel-based bimetallic nanoparticles

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1. Introduction

Nickel based catalysts are well-known heterogeneous catalysts for hydrogenation and reforming reactions. Furthermore, nickel is a good and less expensive alternative to much less abundant materials such as palladium and platinum active for similar reactions. As nickel based catalysts may change their morphology and catalytic performance with respect to the environment, it is essential for the fundamental understanding to investigate the materials under conditions similar to conditions applied during the catalyst lifecycle e.g. calcination, nanoparticle (NP) formation, and catalytic reaction conditions. This study will focus on the NP formation process of Ni-M (M=Cu[1] , Ga[2], and Fe[3]) alloys. The important NP characteristics i.e. crystal structure, morphology, uniformity, and size are investigated for Ni-M (M=Cu, Ga, and Fe) alloys. The characteristics are monitored on the single NP scale as well as over an ensemble of NPs in the same sample. Furthermore, the NP formation process in an intermetallic Ni-M system (M=Ga and Fe) is compared to a substitutional alloy (M=Cu) regarding especially crystal phase composition and purity.

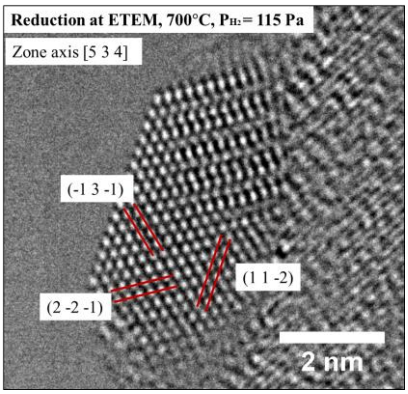

Figure 1. High-resolution TEM image of a Ni_5Ga_3 (δ-phase) nanoparticle acquired in the ETEM under reduction conditions (700°C, 1.15 mbar H_2).

2. Experimental

The studied material systems were synthesized by incipient wetness impregnation method using aqueous solutions of metal nitrate salts as precursor. In the case of NiFe system the impregnation was further developed by using glycerol as solvent. Dedicated complementary techniques were applied to investigate the material systems. In situ X-ray diffraction (XRD) and X-ray absorption spectroscopy(XAS) were used to follow the average catalyst's structural and electronic changes during formation and reaction conditions[1], [2]. High resolution environmental TEM (ETEM) was used to follow the dynamics of the catalysts on the nanoscale (sintering, crystallinity)[1], [2]. Spatially resolved information on the meso scale (50 nm–1 µm) was obtained by X-ray microscopy[4].

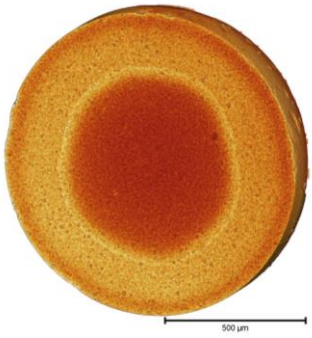

Figure 2. Computed X-ray micro tomography image of reconstructed 3D volume of the Ni-Fe catalyst. The γ-Al_2O_3 sphere is approx. 1 mm in diameter.

3. Results and discussion

At high Ni contents, Cu–Ni samples predominantly form a homogeneous solid solution of Cu and Ni. At lower Ni contents Cu and Ni are partly segregated and form metallic Cu and Cu–Ni alloy phases.
For the Ni-Ga system, highly dispersed Ni(II) nanocrystallites serve as centres for further reduction of the nickel and gallium oxides and metallic gallium is incorporated into the nickel crystal lattice to form an intermetallic phase (Fig. 1).
SEM-EDX and X-ray micro tomography confirmed even distribution of the active Fe-Ni phase throughout the entire volume of the catalyst (Fig. 2). By use of TEM Fe and Ni alloyed nanoparticles with approximately 5 nm were measured.

4. Conclusions

This study illustrates how the formation of NP in Ni-based catalyst have been investigated by in situ diffraction, imaging and spectroscopic methods. The phase purity of the Ni-based NPs in an entire ensemble depends highly on the Ni-M ratio and the complexity of the phase diagram. The results clearly underlined the need for complementary techniques and highlight the potential of these for application in catalysis.

References

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