Complementary EM study on highly active nanodendritic Raney-type Ni catalysts with hierarchical build-up

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Keywords: Raney-type Ni, dendrites, structure, Cs-corrected HRTEM, gas atomisation, slicing view

Nanostructured Raney-type Ni catalysts have been used in industry since the 1920s for the production of a wide range of chemicals. [1] In the EU supported project IMPRESS it has been shown that by using gas atomisation processing high surface area particles with significantly increased catalytic activity in hydrogenation reactions can be produced. [2,3] Structural investigations with complementary methods of electron microscopy in combination with X-ray powder diffractometry have enabled the link between processing, structure and catalytic activity to be explored. [4]

Raney-type Ni catalysts were produced from alloy powder prepared by gas atomisation. After activation by leaching with $NaOH_{aq}$ and prior to the structural investigations the samples were passivated with oxygen. Size selected microparticles of ca. 100 µm size, grown from different melt compositions were chosen for this study.

The microstructure of the samples was characterised in 2D by light microscopy and by SEM, see Fig. 1, and SEM EDX mappings. The nanostructure was investigated with HRTEM and Energy filtered TEM for elemental mappings (Ni, Al) using a Cs-corrected FEI 80-300 Titan microscope operated at 300kV. The use of a dual-beam FIB SEM for sample preparation allowed the investigation of one particular nanodendrite on different scales, first within the microparticle by SEM and hereafter as a single cut lamella in the TEM. In order to correlate the local structure with integral measurements, X-ray powder diffractometry was also carried out. The 3D interconnection of the nanodendrites, which build up the whole particle was imaged with slicing view by using a FIB SEM.

The resulting porous particles were found to be built-up of nanodendrites. The thickness of the dendrites decreases with increasing Al content. The samples with the finest dendrites were obtained from Ni-75%Al alloy powder, i.e. from an alloy with a higher Al content than the one which is used to produce the standard commercial catalysts. The dendrites consist of two adjacent phases, from which one after leaching and passivation is transformed into NiO. This phase is located at the dendrite tips, and

S. Richter, A. Schwedt (Eds.): EMC 2008, Vol. 2: Materials Science, pp. 217–218,
DOI: 10.1007/978-3-540-85226-1_109,

might offer the reactive sites for the catalytic reaction. The complex structure was characterised by Cs-corrected HRTEM. On the mesoscale it shows a polycrystalline framework structure with filled mesopores. The nanocrystals within the mesopores clearly reveal texture. The outer surface of the dendrite tips shows nanosteps, which increase significantly the surface area provided for the catalytic reaction, see Fig. 2.

1. M. Raney: US patent 1563587 (1925)
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4. U. Hörmann, U. Kaiser, N.J.E. Adkins, R. Wunderlich, A. Minkow, H. Fecht, H. Schils, F. Devred, B. Nieuwenhuys, H. Blumtritt, submitted to 9th International Conference on Nanostructured Materials, Nano 2008, Rio de Janeiro, Brazil (2008)

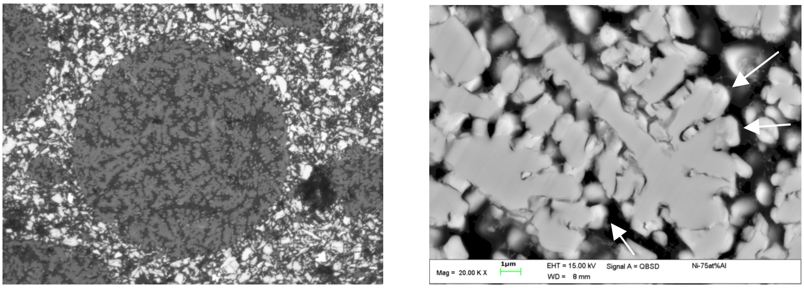

Figure 1. Left: Light microscopy image of a microparticle from the 75 – 106 µm size fraction with a high inner porosity due to the nanodendritic structure. Right: SEM image of a single dendrite with capped tips (light grey), see arrows.

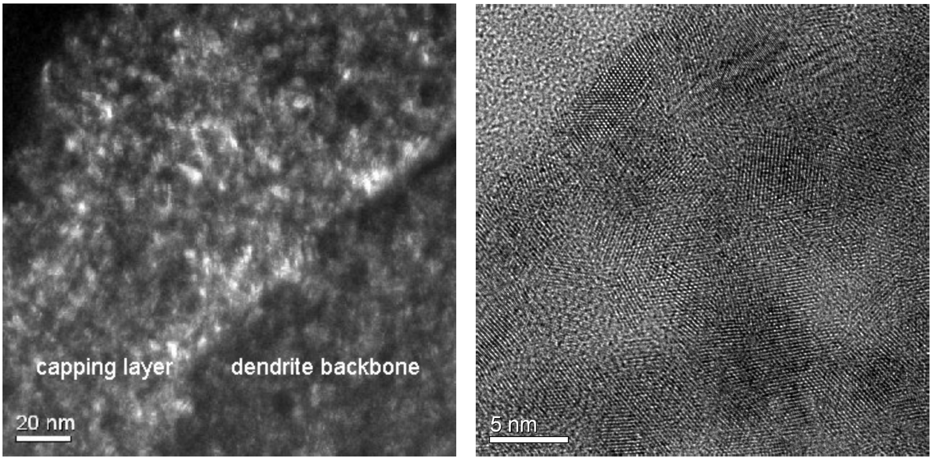

Figure 2. Left: Dark field micrograph of the interface between the caps and the dendrite backbone. Right: Cs-corrected energy-filtered HRTEM micrograph of the mesopores at the outer rim of the capped dendrite tips, showing the pores and the surface steps.