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The FeNi alloyed nanoparticles are a promising alternative to expensive ruthenium-based catalysts for a real-scale application of hydrogen generation by ammonia decomposition[1,2]. In practical applications, millimeter-sized extrudates supports are used as catalysts, where the spatial distribution of the active phase should match with the type of reaction [3]. In this work, a novel synthesis route was developed for the preparation of a FeNi/Al_2O_3 egg-shell catalyst [4]. Egg-shell is a preferred profile considering the highly endothermic nature of ammonia decomposition reaction. The high viscosity of glycerol, used as a solvent, prevents the fast migration of the FeNi active phase solution towards the inner-core of Al_2O_3, giving control over the large capillary pressures during impregnation. The distribution profiles were analyzed at macroscopic scale through scanning electron microscopy mapping (SEM-EDX) and optical microscopy (Figure 1). A three-dimensional (3D) reconstruction of the spherical-shaped Al_2O_3 was achieved using x-ray micro tomography and the FeNi egg-shell spatial distribution was inspected throughout the entire volume of the support body. Transmission electron microscopy (TEM) and scanning TEM (STEM) analysis of ultrathin lamellas (< 20 nm) carved from the outer-shell region established the presence of FeNi alloy nanoparticles with a size of approximately 5 nm (Figure 2). The egg-shell catalyst showed significant higher activity in ammonia decomposition by converting 3 times more ammonia to equilibrium conversion than either egg-white or catalyst with uniform distribution.

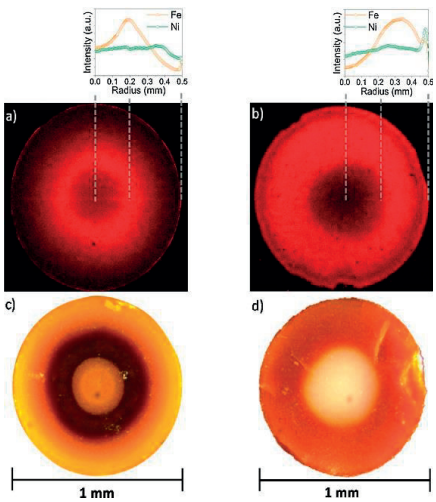

Figure 1. (a) SEM-EDX elemental maps of Fe for the FeNi/Al_2O_3 catalysts prepared from an aqueous solution of the active phase and (b) from a glycerol solution. Optical microscopy images of the aforementioned samples, (c) impregnation with an aqueous solution, and (d) with glycerol.

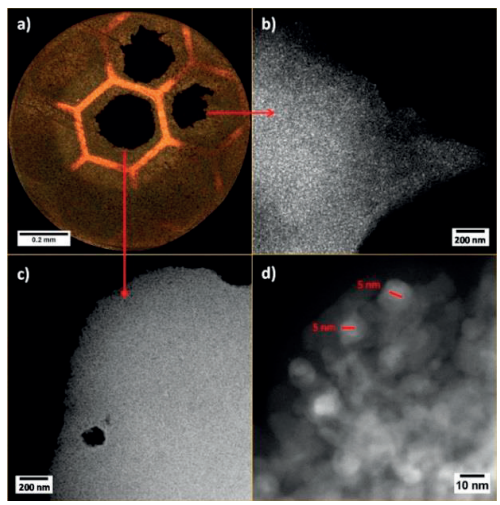

Figure 2. (a) Optical microscope image of a TEM specimen prepared from an egg-shell catalyst placed on a Cu hexagonal grid. HAADF-STEM images obtained from the Fe–Ni rich outer-shell (b) and the core (c) of the γ-Al_2O_3 sphere (d) High-magnification STEM image of the egg-shell catalyst acquired from the Fe–Ni rich outer-shell.

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