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Structure-activity investigation of Ni-Ga model catalysts for CO₂ hydrogenation to Methanol

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Metal nanoparticles (NPs) dispersed on a high surface area support are widely used as catalysts for heterogeneous catalysis. The atomic structure of the active NPs is highly linked to the performances of the catalyst. An Environmental Transmission Electron Microscope (ETEM) equipped with a differential pumping system to confine a controlled gas flow around the specimen, offers a unique tool to investigate individual NPs at the atomic level in a gaseous environment [1]. Nevertheless, the morphology of the high surface area support tends to complicate the interpretation of TEM micrographs on the atomic level and blurs the spectroscopic information due to limited depth of field and multiple scattering events. One way to circumvent this is to synthesize NPs on a low surface area support representing the “real” high surface area supported catalyst.

δ-Ni₅Ga₃ catalysts prepared by incipient wetness impregnation on a high surface area SiO₂ support (Figure 1A), have shown promising for CO₂ hydrogenation to methanol with comparable turn-over frequencies to the preferred commercial Cu/Zn/Al₂O₃ catalyst system[2-3].

This study presents ETEM investigation of Ni-Ga NPs dispersed on ~200 nm SiO₂ spheres. The catalyst shows similar size distribution and activity pr. surface area as the low-surface area supported catalyst.

The SiO₂ spheres supported model catalyst features numerous NPs that can be illuminated directly with the electron beam (Figure 1B). This enables atomic resolved structural (HRTEM) (Figure 1C) and spectroscopic information (EELS) of the individual NPs.

The catalyst formation process and pre-dominant deactivation mechanism at the atomic level are investigated in the ETEM by following the morphology (surface structure, facets, NP size, crystal structure, material composition) during catalyst synthesis and CO₂ hydrogenation to methanol. The investigation is supported by complementary techniques such as in-situ X-Ray Diffraction (XRD) and catalytic activity measurements (fixed-bed reactor) using a Gas Chromatograph (GC) and a Mass Spectrometer (MS).

Figure 1. TEM micrographs of NiGa NPs supported on A) High surface area SiO₂ support B) Ni-Ga NPs on ~200 nm SiO₂ spheres, and C) HRTEM micrograph of Ni-Ga NPs on top of SiO₂ spheres ( P(H₂)=110Pa, T=700°C).

References