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TEM characterization of Ni-Ga intermetallic catalysts for hydrogenation of CO_2

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Introduction

Nanostructured intermetallics dispersed on high surface area supports are assuming increasingly importance within the heterogeneous catalysis field. The atomic structure of the active NPs is highly linked to the performances of those catalysts that seems to behave differently compared to their relative single-metal NPs. This study presents local and structural investigation of Ni-Ga NPs dispersed on ~120 nm SiO_2 nanospheres. The catalyst shows similar size distribution and activity pr. surface area as the high-surface area supported catalyst confirming that the system is reliable in terms of catalytic behavior. 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 during in-operando conditions of the catalyst [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 reduce the complexity of the mesoporous high-surface area support by developing low-surface area (non-porous) supports that consist of nanosized SiO_2 spheres. 2D model catalysts has also been developed by synthesizing the NPs on 20 nm thick membranes [2].

Materials and Methods

The catalyst formation process and reaction at the atomic level are investigated in the ETEM by following the morphology change (surface structure, facets, NP size, crystal structure, material composition) during NPs formation and CO_2 hydrogenation to methanol. Different chemical synthesis have been performed to prepare δ-Ni_5Ga_3 catalysts on a high and low surface area SiO_2 support. The investigation is supported by complementary techniques such as *in-situ* X-Ray Diffraction (XRD) and activity tests coupled with Gas Chromatograph (GC) and a Mass Spectrometer (MS).

Results and Discussion

SiO_2 spheres supported model catalyst features numerous NPs that can be illuminated directly with the electron beam (Figure 1) enabling atomic resolved structural and investigation on local chemical compositions. XRD shows the active δ-phase of the NiGa catalyst upon reduction in pure hydrogen at T=700°C. Normalizing by the surface area of the catalyst we find comparable activities between high-surface and low-surface area supported catalyst (Figure 2).

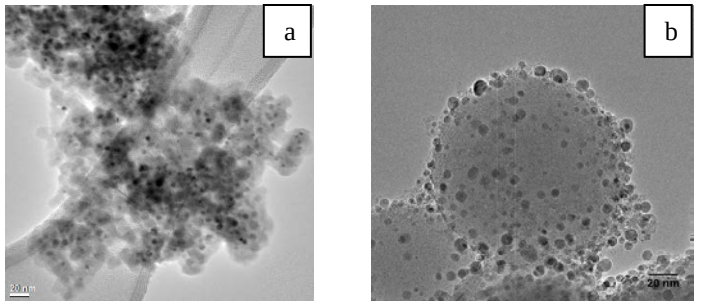

Figure 1. ETEM micrographs of NiGa NPs supported on: a) high-surface mesoporous SiO_2 powder; b) 150 nm SiO_2 spheres, $P_{(H2)}$=115 Pa, T=700°C.

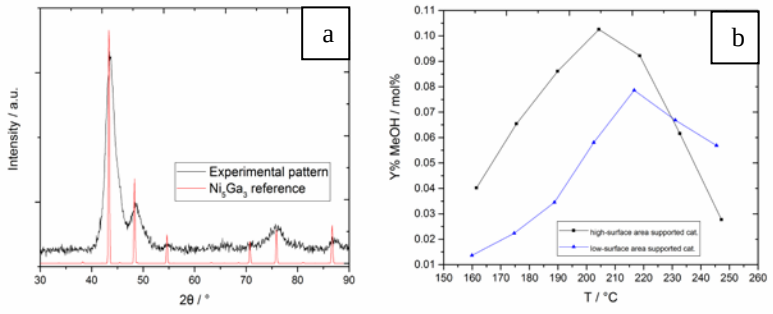

Figure 2. a) XRD pattern of NiGa/SiO_2 powder after reduction at 700° C in pure H_2 ($P_{(H2)}=10^5$ Pa); b) activity test during methanol reaction over NiGa/SiO_2 catalyst for high-surface area (black) and low-surface area (blue) SiO_2 supports. Reaction conditions: 75 mL/min of H_2 + 25 mL/min of CO_2, P = 10^5 Pa, T=180-250°C.

Significance

The optimized Ni-Ga catalyst is promising for CO_2 hydrogenation to methanol with comparable activities to the preferred commercial $Cu/Zn/Al_2O_3$ catalyst system [3-4].

References

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