Insight into the structure of SiO_2-supported Ni-Ga nanoparticles for catalytic application via X-ray absorption spectroscopy and total scattering

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To close the carbon cycle, the direct hydrogenation of CO_2 to methanol (CH_3OH) plays a key role allowing to convert a major greenhouse gas into a valuable energy carrier and platform chemical.[1] Supported bimetallic catalysts are gaining increasing attention for CO_2 hydrogenation reaction due to the possibility of tuning their catalytic properties by judicious choice of the ratio of the alloying elements. The development of highly active and selective catalysts for CO_2 hydrogenation relies hence on obtaining a fundamental understanding of the relationship between a catalyst's structure and its activity. However, heterogeneous catalysts are complex systems, typically composed of various phases and sites that exhibit different functionalities which requires the use of multiple and complementary techniques for their characterization. [2] X-ray absorption spectroscopy and atomic pair distribution function analysis (PDF) of X-ray total scattering data can provide detailed information on the structure of bimetallic supported nanoparticles. XAS, being element selective, allows to study the electronic state and geometry of each metal via XANES analysis (X-ray absorption near edge structure analysis) and their local atomic structure between ~1-5 Å by EXAFS (extended X-ray absorption fine structure) analysis. Probing the longer-range order (i.e. above ca. 5 Å) via EXAFS analysis is however challenging. PDF can interrogate the local to nanoscale structure of supported bimetallic nanoparticles, extending substantially the atomic length scale that can be studied, from ~1 Å up to several nanometers. In this presentation, we will show how XAS (Ni and Ga K-edges) and PDF analyses provide structural information of a series of Ni_xGa_y nanoparticles supported on SiO_2 (total metal loading of ca. 5 w.%). The PDF analysis was performed via a so-called differential PDF approach, i.e. subtracting the signal of the SiO_2 support and, thus, allowing us to characterize the nanocrystalline phases (disordered or intermetallic alloys) of the supported nanoparticles. Ga K-edge XANES and EXAFS reveal the presence of GaO_x species while Ni XANES and EXAFS confirm the presence of Ni^0. Thus, combining the information obtained via XAS and PDF techniques is highly important to obtain a full atomic to nanoscale description of heterogeneous catalysts.

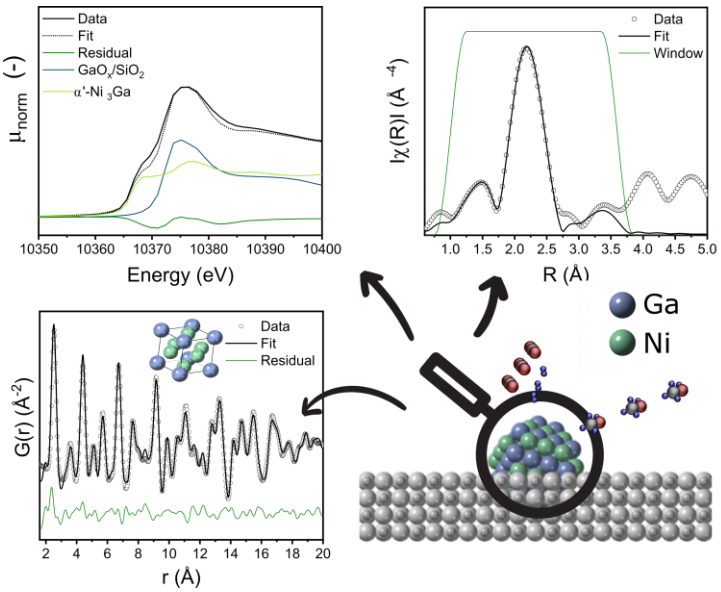

Figure 1. Top: Ga K-edge XANES and EXAFS of α'-Ni_3Ga/SiO_2. Bottom: Differential X-ray pair distribution function fitted to the α'-Ni_3Ga structure.

[1] G. A. Olah, Angewandte Chemie International Edition 2005, 44, 2636-2639.

[2] A. Tsoukalou, P. M. Abdala, D. Stoian, X. Huang, M.-G. Willinger, A. Fedorov, C. R. Müller, J. Am. Chem. Soc. 2019, 141, 13497-13505.

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