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Advanced and *In-Situ* Electron Microscopy Investigation of Phase Composition and Phase Transformation in Ga-Rh Liquid Metal Catalysts

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Supported Catalytic Active Liquid Metal Solutions (SCALMS) have been recently demonstrated to be a highly promising class of heterogeneous catalysts, which show superior activity, robust performance and selectivity in dehydrogenation reactions [1]. At typical dehydrogenation temperatures of 500 °C, it is conceived that the large surface to volume ratio of the nano-droplets of the liquid metals, supported in the open meso- or macroporous scaffold, provide huge number of catalytically active sites which are intrinsically robust to coke formation and degradation due to the highly dynamic nature of the liquid metal alloy. Such liquid metal nanoalloys are intermetallic compounds of low-melting host elements (e.g., Ga, In) with small amount of catalytically active transition metal elements. These intermetallic compounds typically have complex stable crystal phases in solid state. The structural information, particularly the phase stability of the nanoalloys, is indispensable to render the full picture of their catalytic performance, which is however hardly accessible with catalytic tests and require a combination of *in situ* surface science, scattering and high-resolution imaging and spectroscopy techniques.

In this work, we study the structure, composition and phase stability of model Ga-Rh systems with advanced transmission electron microscopy (TEM), both static at room temperature and *in situ* during heating/cooling. The Ga-Rh nanoparticles are deposited on a SiO_x membrane via physical vapor deposition with Rh concentration ranging between 0.6 and 6 at.%. At room temperature, a typical two-phase microstructure of crystalline (c-) precipitates embedded in amorphous (a-) nanoparticles is found in all studied samples. By combining information from EDXS, HRTEM and careful analysis of electron diffraction patterns, the crystal phase is identified as $Ga_{16}Rh_3$ or $Ga_{21}Rh_4$ and their derivatives (cf. Fig. 1a-d). *In situ* observation while heating the samples in the TEM was performed to elaborate the phase stability of the c-Ga_xRh_y/a-GaRh nanoparticles, since the phase diagram of the Ga-Rh system is not safely established in the low Rh concentration range. Low-dose electron diffraction has been performed in order to minimize the beam effect as identified during *in situ* imaging experiments. Disappearing of sharp crystal rings is observed at elevated temperature, which is then followed by the fade-out of the second broad diffuse ring (cf. Fig. 1e), indicating a solid-liquid phase transformation. Higher Rh concentration show higher transformation temperature. These results shed light on the microscopic mechanisms underlying the high performance of Ga-Rh SCALMS in propane dehydrogenation.

References:
[1] Taccardi, N. et al. Nature Chemistry **9**, (2017) p.862.
[2] M.W. and E.S. acknowledge financial support by DFG via research training group GRK 1896 “In-situ Microscopy with Electrons, X-rays and Scanning Probes”.

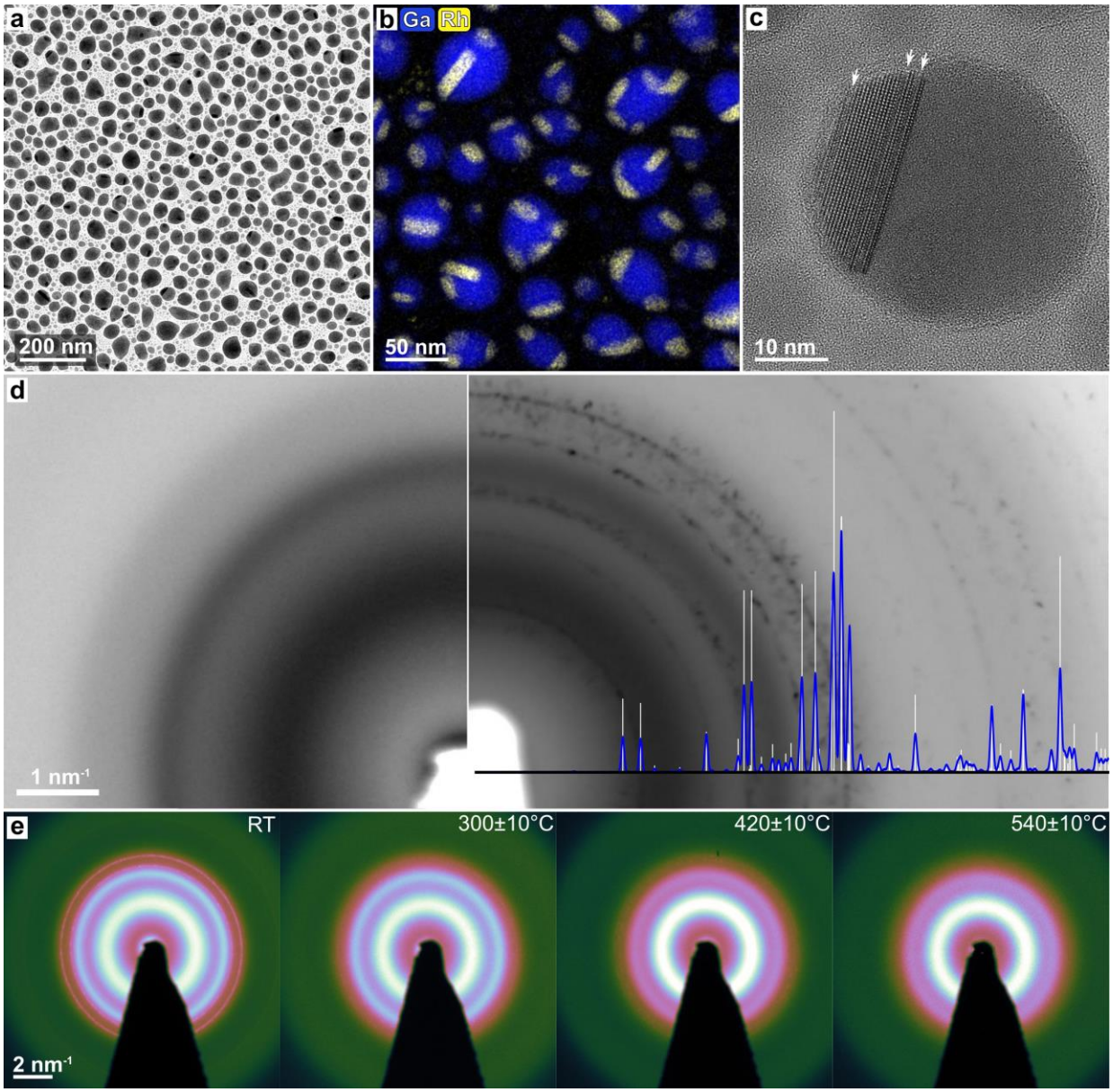

Figure 1. Structure, composition and temperature-dependent phase properties of Ga-Rh nanoparticles. (a-d) Results obtained from a sample with average Rh = 2.7 at. %. (a) BF-TEM image of the nano-particles on thin SiO2 membrane. (b) EDXS composite map of Ga and Rh, confirming an increased Rh concentration (~ 12 - 15 at. %) at the precipitates. (c) HRTEM image of a single nano-particle. The arrows indicate stacking disorder. (d) Zero-loss filtered electron diffraction pattern of pure amorphous Ga (left half) and with Rh = 2.7 at. % (right half). The kinematic powder diffraction intensities (white lines) and calculated nano-crystalline diffraction intensities with $Ga_{16}Rh_3$ phase (ICSD No. 415871) are superimposed on the right half. (e) Few key frames of (elastically filtered) electron diffraction patterns taken during an *in situ* heating experiment from the samples with Rh = 0.9 at. %. Temperatures are indicated at top-right corner of each pattern. Sharp crystal peaks fade out at ~300ºC, while the second broad ring reduce its intensity at ~330ºC, suggesting a solid (amorphous) to liquid phase transition.

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